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PHYSICAL REVIEW.

ON THE SPECIFIC HEAT OF GASES AT HIGH TEMPERATURES.[1]

By L. Holborn and L. W. Austin.

THE specific heat of gases at constant pressure was first successfully determined by Regnault.[2] His observations covered the temperature interval from $-30°$ to $+210°$ C. and pressures from 1 to 12 atmospheres. He found that the specific heats of the simple gases, air, oxygen and hydrogen were independent both of temperature and pressure within the limits of the observations. The specific heat of carbon dioxide, on the other hand, when measured between 0° and 200° showed a well marked increase with increasing temperature.

E. Wiedemann,[3] who repeated the experiments of Regnault on a smaller scale, arrived at similar conclusions. Witkowski,[4] investigating air at low temperatures, between 100° and $-170°$, also found the specific heat constant. On the other hand he found that it increased with increasing pressure (up to 70 atmospheres) and that this increase rose with decreasing temperature. An increase of specific heat with increasing pressure has also been observed by Lussana[5] between 0° and 200° in the case of air, oxygen and carbon dioxide.

[1] Translated from Abhandlungen der Phys.-Tech. Reichsanstalt, Vol. IV., Heft. 2, p. 133, 1905.

[2] V. Regnault, Relation des exper., 2, 1862.

[3] E. Wiedemann, Pogg. Ann., 157, p. 1, 1875.

[4] A. Witkowski, Journ. de phys. (3), 5, p. 123, 1896.

[5] S. Lussana, Cim. (3), 36; (4), 1, 3, 6, 7, 1894–98.

The specific heat at constant volume has been measured by Joly[1] who enclosed the gases (air, hydrogen and carbon dioxide) under high pressure in hollow copper spheres and determined their specific heats between room temperature and 100° by means of the steam calorimeter.

In addition, the mean specific heat at constant volume between 0° and a high temperature has been measured by means of explosion experiments, by Mallard and Le Chatelier[2] (1300° to 2800°), by Berthelot and Vieille[3] (2800° to 4400°) and recently by Langen[4] (1300 to 1700°).

METHOD OF OBSERVATION.

All the observers who have measured the specific heat at constant pressure have made use of the method of mixtures of Delaroche and Berard.[5] The gas first flows through a tube system surrounded by a bath of some liquid where it is heated to the desired temperature, and finally flows out through a second tube system surrounded by the water of the calorimeter where its heat is given up. The temperature at which the gas enters the calorimeter is determined by means of a thermometer in the heating bath, and the temperature at which it leaves is given by the thermometer in the calorimeter, experiments having been made to show that the gas actually assumes the temperatures of the heating bath and of the calorimeter as it passes through them.

The connection between the heating bath and calorimeter must be made as short as possible in order that the gas may enter the latter with the least possible loss of heat in transit. There is, however, always a heat loss at this point, the influence of which can be made negligible only by using powerful gas currents. Regnault took great pains in the investigation of this source of error. In his experiments with air he varied the flow of gas between wide limits increasing it until the value of the specific heat became independent

[1] J. Joly, Phil. Trans. (A), 182, p. 73, 1891; 185, pp. 943 and 961, 1894.

[2] Mallard and Le Chatelier, Ann. des mines (8), 4, p. 274, 1883.

[3] Berthelot and Vieille, Ann. de chim. et de phys. (6), 4, p. 13, 1885.

[4] Langen, Forschungsarbeiten, herausgegeben vom Ver. Deutsch. Ing., Heft 8, p. 1, 1903.

[5] Delaroche and Berard, Ann. de chimie, 85, p. 72, 1813.

of the quantity per minute. In the calculation of the specific heat a correction must be made to the observed rise in temperature of the calorimeter. This is due partly to the radiation of the calorimeter and partly to the heat conducted to it from the heating bath through the connecting tube. The first portion, which is common to all calorimetric measurements, can be controlled by choosing a suitable initial temperature for the calorimeter, while the second can be kept within the necessary bounds by introducing bad conducting material in the connection between the calorimeter and heater. By observing the course of the calorimeter temperature before and after the passage of the gas this correction is determined. It is nevertheless doubtful whether with the Regnault arrangement the flow of heat due to conduction does not change when the gas current sets in. The question can be investigated only indirectly, by varying the strength of the gas flow.

Witkowski varied the above method of measuring the gas temperature by making use of a thermoelement protected from radiation, which could be brought close to the opening of the calorimeter. In the present investigation which has for its object the determination of the specific heats at high temperatures this method has also been used. For the heating of the gases however baths were discarded as they are not convenient above 500°.

Arrangement of Apparatus.

The Heating Tube. — The gas was heated electrically in a nickel tube *A*, 1.2 m. long 8 mm. inner diameter, and of 1 mm. wall thickness, on which was wound a coil of nickel wire. The windings were insulated from the tube by asbestos and from each other by clay put on wet. Outside this was a second layer of asbestos, and the whole was inclosed in a porcelain tube. The gas was introduced at one end and was heated in the coarse nickel filings with which the tube was filled according to the plan of E. Wiedemann. At three-fourths the length of the tube it encountered a dividing wall soldered in with silver and was led out through a side tube 25 mm. long and 4 mm. in diameter into the calorimeter. In this way the influence of the cool end of the tube was eliminated. Otherwise the gas in passing through the cool portion gives up so much of its heat

that its temperature varies in a marked degree with the strength of the flow.

Opposite the outlet tube W a second nickel tube B (25 cm. long, 4 mm. diameter) was joined to the heating tube and through this a platinum platinum-rhodium thermo-element T was introduced. This passed through the heating tube A which at this point was kept

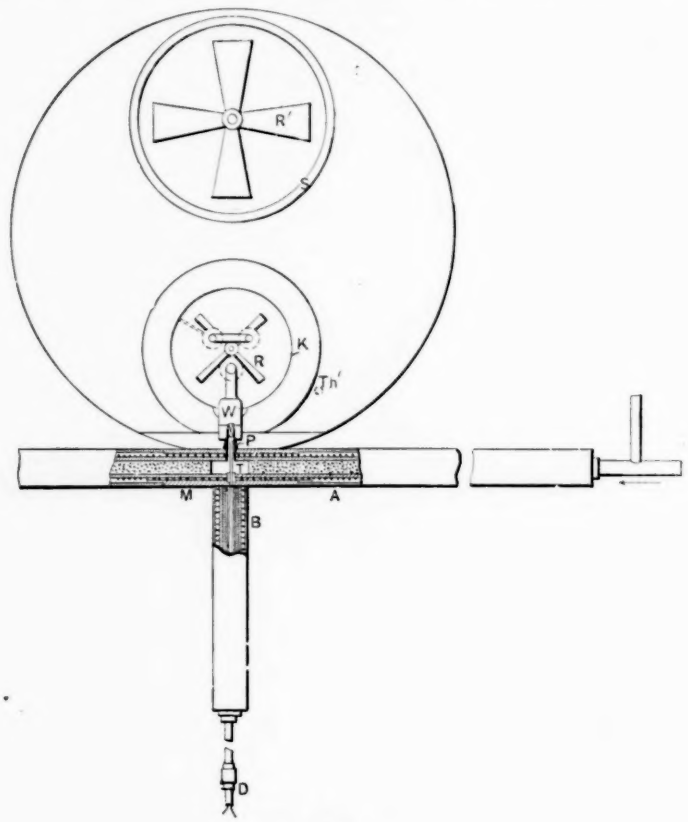


Fig. 1.

free from nickel filings by the dividing wall M on one side and a disk of wire net on the other. The thermojunction lay in the outlet tube W, 1 cm. from its free end. In this space a thin silver band bent in the form of a screw was inserted to prevent radiation of the thermojunction to the cool calorimeter. The thermoelement consisted of wires 0.25 mm. in diameter which were insulated through

the greater part of tube *B* with thin porcelain tubes. In the portion near *A*, in *A* itself and also in *W*, the insulation consisted of thin quartz capillaries lying close together and wrapped about with platinum band 0.01 mm. in thickness. The thermojunction which was hardly thicker than a single wire was free from quartz and was nsulated from the platinum sheath by an air space. Special car was taken that the end of the thermoelement should not come in contact with the tube wall. In one portion of the work this was

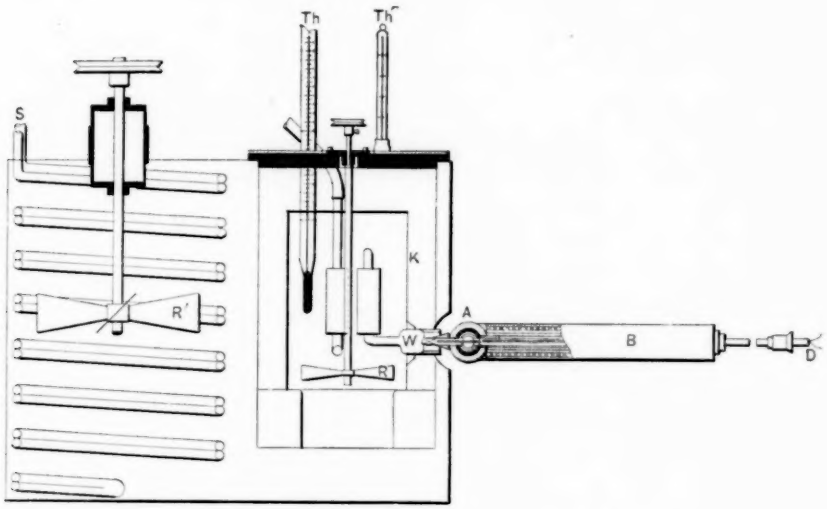


Fig. 2.

attained by supporting the flexible end of the element on a bit of mica of the same width as the diameter of the tube. The platinum band which was intended for the protection of the thermoelement from radiation from the tube wall also served to protect the quartz from the nickel oxide which was carried along with the gas current in minute quantities from the heating tube. Otherwise this after a time became opaque and disintegrated.

The wires of the thermoelement were insulated from the tube *B* by a porcelain tube which passed out through a rubber stopper at *D*, in which it could be moved back and forth when it was desired to determine the temperature at different points in the tube *W*. The end *D* of the tube always remained cold enough so that the wires could be sealed into the end of the porcelain tube with sealing wax.

A secondary heating coil of nickel wire wound on porcelain 12.5 cm. long and insulated like the main coil was placed on the tube B to compensate for the loss of heat by conduction through the two side tubes and for the loss of one turn of wire on the main coil where the side tubes were attached.

The Calorimeter. — The calorimeter K of about 0.5 liter capacity was made of pure silver 0.5 mm. thick (Figs. 1 and 2). In its center were situated three silver tubes 1.5 cm. in diameter filled with silver filings and connected by 0.6 cm. silver tubes. These absorbed the heat from the gas as it passed through. That the gas actually issued from the calorimeter at calorimeter temperature even when heated to the highest point (800°) was made certain by experiments with a constantan copper thermoelement.

A thermometer *Th* with inclosed scale divided in 0.1° and read by means of a telescope served for the measurement of the specific heat. A small stirrer R insured the rapid and regular taking up of the heat of the silver tubes by the water. The weight of the calorimeter including the tubes and filings was 247 g.

The calorimeter was surrounded by a copper water jacket and was placed at one side instead of at the center of this in order that the heating tube might be brought as close to the calorimeter as possible. The water jacket had a capacity of 15 liters. The temperature of this tended to rise slowly due to the radiation from the heating tube. To obviate even this slow change a spiral tube was introduced into the jacket through which cold water from the house system flowed. The quantity of water required for any given heating tube temperature was regulated according to the readings of a water manometer. By this means the jacket temperature indicated by the thermometer *Th'* was kept constant during the time required for an experiment to 0.1°. This temperature was generally about 18°. The water in the jacket was stirred by a stirrer R' driven by the same electric motor used for driving the calorimeter stirrer R.

In former researches the connection between the calorimeter and heating apparatus was made by means of cork. This material is not usable however much above 200°. In our work the means of connection consisted of a specially made porcelain tube shown

in natural size in Fig 2, *a*. The larger end of this was inserted in the mouth of the system of tubes of the calorimeter while the other end fitted over the tube *W* reaching as far as the windings of the heating tube *A*. Both the joints were made tight by firmly packed asbestos.

The Gases. — The gases for the investigation were taken directly from ordinary commercial cylinders. Before entering the heating tube the gas passed through a glass tube 1.5 m. long filled with calcium chloride. The strength of the gas stream was regulated with sufficient accuracy by means of an ordinary reducing valve, the pressure read on a mercury manometer before the gas entered the heating tube, remaining constant to 1 mm. Only in the case of carbon dioxide was it found necessary to regulate during the experiment. This was evidently due to the changes in the valve temperature resulting from the evaporation of the liquefied gas. The gas entered the heating tube *A* under an excess pressure of about one-half atmosphere which was necessary on account of friction on the nickel filings which increased with the temperature. For overcoming the friction in the system of tubes in the calorimeter only a pressure of from 1 to 2 cm. of mercury was required, as was established by special experiments. No heat due to the friction of the gas on the filings in the calorimeter was observed.

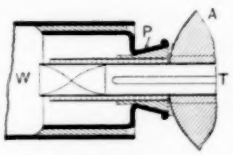


Fig. 2, *a*.

The Gasometer. — The quantity of gas was measured after it left the calorimeter. The gasometer which served to hold and measure the gases is represented in Fig. 3. The gas passed first through a spiral cylinder S_1 and then entered a rubber bag *G* which hung in a closed zinc cylinder. From this a quantity of air, equal in volume to the gas entering the rubber bag, was forced through the tube *L* into the vessel *F* out of which water was expelled through the opening *Q*. This was caught in a pail and afterwards weighed. By this arrangement gas left the calorimeter under a constant pressure differing only a little from the pressure of the atmosphere. The presence of the rubber bag guarded against the possibility of absorption by the water, of the gases measured, since only the

air from the zinc cylinder came in contact with the water. There was no difficulty in determining the volume of CO_2 with this arrangement as the diffusion of this gas through the rubber during the short time required for an experiment could be neglected.

The zinc cylinder Z and the vessel F were kept at the same temperature. To this end the cylinder was placed in a large bath the water of which was continually renewed from the water system of the laboratory, while the vessel F which was surrounded with a layer of cotton covered with oil cloth, was filled through the funnel N from the same source before each experiment.

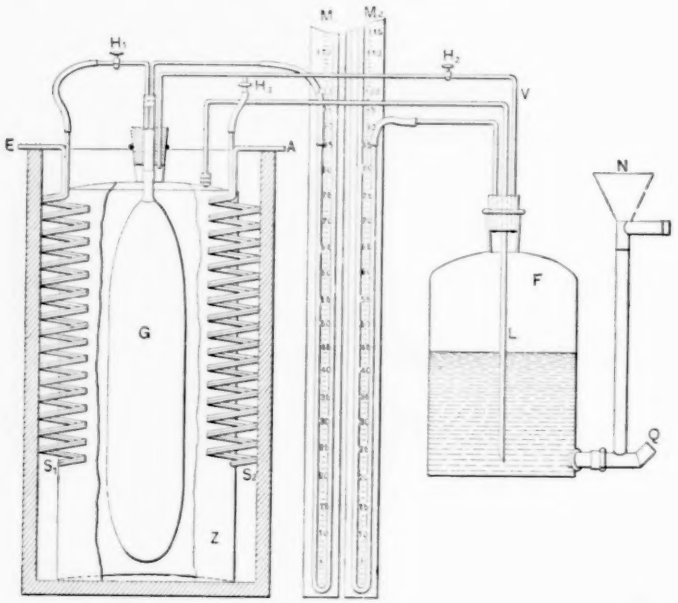


Fig. 3.

Since the gas passed through the copper spiral S_1, situated in the same bath with the zinc cylinder Z before entering the rubber bag, it was not necessary to wait long for it to attain the bath temperature. This otherwise would have consumed considerable time as the quantity of gas was usually about 20 liters. Before the first experiment each day it was necessary to wait for some time after filling the bath until the air in the zinc cylinder had completely assumed the bath temperature. This never varied more than 1° during the day.

After each experiment the air was generally forced back from the vessel F into the cylinder Z. This was accomplished by closing the opening Q and the cock H_3 and opening H_2 and H_1. Water was then poured in through N, and the air passed through the tube V and at the same time forced the gas from the rubber bag out through H_1. Air could be introduced into the zinc cylinder also through the cock H_3, being brought to the temperature of the bath by passing through the spiral S_2. Ordinarily this opening was used only to bring Z to atmospheric pressure. The pressure of the gases in G and F was read on the water manometers M_1 and M_2. G was brought to atmospheric pressure before each experiment and again after the entrance of the gas. This was accomplished after the closing of the cock H_1 by opening H_2 for a moment so that a little air flowed from Z to F through the tube V.

Letting M denote the weight of the displaced water in kgs., T its temperature (which differed only a fraction of a degree from the temperature of the zinc cylinder), H the pressure (mm. Hg) in the vessel F, which was given by the readings of the barometer and the manometer M_2, the mass m (in grams) of the gas contained in the rubber bag is

$$m = M \frac{H}{760} \frac{s}{1 + \alpha t},$$

where α is the expansion coefficient and s the weight (in grams) of 1 liter of gas at 0° and 760 mm.

The Gas Temperature. — The temperature of the gas was measured just before it entered the calorimeter with the thermoelement already described. Details regarding its use have been given in a former paper by one of the authors.[1] For the sake of certainty new wires were made use of since those which have been already used immersed to a considerable depth in a heated region sometimes cease to be homogeneous in the neighborhood of the junction. This can easily lead to errors when, as in the present case, the wires are heated only close to the junction.

After many preliminary experiments in which among others the thermoelement was surrounded by a silver tube insulated from the

[1] L. Holborn and A. Day, Ann. d. Phys. (4), 2, p. 538, 1900.

walls of the tube *W* through which the gas entered the calorimeter, we finally heated the tube *W* by means of a coil of 0.2 mm. platinum wire. This was wound on a thin layer of asbestos paper in bifilar winding so that the two free ends came out together from the porcelain tube *P* close to the heating tube *A*. Toward the calorimeter the windings were brought closer together so as to produce as nearly as possible a uniform temperature throughout the tube *W*. The current in the platinum coil was regulated so that the thermojunction indicated the same temperature of the flowing gas when it was displaced to different points along the tube *W*. Then, since in the actual measurements the junction always lay close to the screw-shaped silver plate, it followed that as soon as the gas flowed the whole of the thermoelement was at the same temperature as far as the point where it entered the tube *B*. Before and afterward the readings were lower, but rose at once as soon as the cock of the gas cylinder was opened, and remained constant in general during the whole time that the gas flowed. Only in the case of the highest temperature was there a slight fall when the flow continued for some time, evidently caused by the fact that the heating tube *A* did not have sufficient heat capacity and gradually cooled during the course of the experiment.

The temperature of the gas as measured in this way before its entrance into the calorimeter, is exactly determined by the condition of the heating tube. Within wide limits it is independent of the quantity of gas flowing in unit time, when the same current is sent through the heating coils. The kind of gas is also of little influence. Even at 800° carbon dioxide gave only about 6° lower temperature than air and nitrogen. If it is desired only to compare[1] the specific heats of different gases at the same temperature, if we assume that the known specific heat of one of the gases does not vary with the temperature, the thermoelement could be removed and the temperature be determined by the change in calorimeter temperature produced by the passage of the standard gas. It is then only necessary to keep the strength of the heating current constant and to regulate

[1] E. Wiedmann made measurements on the specific heat of different gases above 100° in a similar way, heating his heating tube in an air bath and assuming that air remained constant between 20° and 200°.

the quantities of the other gases so that each imparts about the same quantity of heat to the calorimeter.

It was found also that the ratio of the specific heats of the different gases was the same when the above mentioned silver tube was used and the side tube *W* not heated. The Regnault arrangement was also tried with success for measurements of this kind at 220°. From all this it is seen that an electrically heated tube for heating the gas can completely take the place of liquid baths, and that it is superior in ease of adjustment and constancy and in being applicable to higher temperatures. The only disadvantage is that the electric oven has a small heating capacity, this being about the same as that of an air bath. The current for the coil of tube *A* was taken from a battery of accumulators the voltage of which could be varied as desired. The coil *B* was in a shunt which in the beginning had to be regulated for each temperature. The small coil on the side tube *W* was connected to a battery of small accumulators and the current for each temperature regulated in preliminary experiments.

The amount of gas which could be used in each experiment was limited by the capacity of the gasometer, which was about 25 liters. Since carbon dioxide has the greatest specific heat per unit volume, it was used in the experiments for determining the dependence of the results on the velocity of the gas current. This influence was found to lie within the limits of the errors of observation. Ordinarily the gas was allowed to flow for four minutes, and the quantity was frequently increased or diminished by increasing or diminishing the velocity.

The Calorimeter Temperature. — The heat which the calorimeter received from without, coming for the most part from the heating tube through the small tube used for introducing the gas, necessitated a correction which was determined in the usual manner from observations on the change of temperature in the calorimeter for periods of ten minutes before and after the experiment. The readings on the thermometer in the calorimeter, which were always taken with rising temperature, lay between 3° below the water jacket temperature and about 10° above it. For our purposes it is allowable within these limits to make a linear interpolation of the correction during the time required for the experiment itself. We

proved this both by plotting a curve for the correction from readings extending over the whole range of temperature, and also by imparting a definite amount of heat per unit time to the calorimeter from an electrically heated coil immersed in the water, beginning with different initial temperatures. The temperature of the heating tube was about 450° and the rise in the calorimeter temperature in the first and last periods varied between 0.13° and 0.06° per minute. During four minutes current was sent through the coil in the calorimeter so that the temperature rose about 4°, first at a mean calorimeter temperature of 19°, and then at 25°. The difference between the two results was on an average less than 0.2 per cent. In these experiments the calorimeter was slower in changing its temperature than in the experiments with gases where of course the small heating coil was absent. This, on account of the insulation of the wires, gave up its heat more slowly than the silver tubes. The cooling of the heated calorimeter before a new experiment was accomplished as follows: The water was first completely sucked out through the opening left for the thermometer. As the bottom of the calorimeter was curved all the water could be removed except that adhering to the walls. Then a fresh quantity of water of suitable temperature measured at 15° in a half-liter flask, was poured in. Before the calorimeter was connected to the heating tube it was proved by weighing that this procedure insured the constancy of the quantity of water to about 0.1 gram. The water equivalent of the calorimeter with its stirrer (except the portion above the glass insulator set in the spindle just above the calorimeter) and thermometer was 15.7 grams. The quantity of water was 499.6 grams so the sum

$$w = 515.3 \text{ g.}$$

Calling m the weight in grams of the gas entering the calorimeter, with the temperature θ_1, and ϑ' the resulting rise in temperature of the calorimeter, which is derived from the observed change in temperature ϑ by applying the correction k due to the heating by conduction, etc., and calling c the mean specific heat of the gas at constant pressure, and θ_2 the mean calorimeter temperature during the passage of the gas, then

$$w\vartheta' = cm(\theta_1 - \theta_2).$$

Observations.

The observations contained in the following tables were taken at three different temperatures of the heating tube, t_0 denotes the temperature of the calorimeter jacket, z the time of passage of the gas in minutes, τ_1 and τ_2 the mean change in the calorimeter temperature per minute during the periods before and after the passage of the gas. The order in which the observations were taken is shown by the dates.

It was in general so arranged that each gas was experimented upon at different times as a test of the constancy of the apparatus This was necessary inasmuch as the apparatus was several times taken apart, the insulation of the thermoelement renewed, and its junction often moved forward and back in the region of uniform temperature already mentioned. The differences were naturally smaller when the apparatus remained undisturbed. Changes in the gas temperature on the same day were generally caused by gradual decrease in the current strength in the heating coils. The increase in the calorimeter temperature ϑ is always calculated for one minute longer than the time of passage of the gas. The slower rise of temperature due to conduction from the heating tube, etc., set in regularly within one half minute after the gas ceased to flow. The regulating valve and mercury manometer allowed the gas current to be kept so constant that the temperature of the calorimeter rose regularly during the passage of the gas, which was clearly shown by the thermometer readings taken every half minute. Before and afterwards the thermometer was read each minute.

Observations were taken at three different gas temperatures, that is at 440°, 630° and 800°. An upper limit was placed to this temperature by the danger of melting the silver soldering of the nickel tube, and a lower limit by the uneven distribution of the temperature in the heating tube and the decreased sensibility of the thermoelement. The use of the same calorimeter for a given quantity of gas is advantageous only for a limited interval of temperature.

Oxygen was the least pure of the gases used. According to the analysis of the chemical laboratory of the Reichsanstalt it contained 9.5 per cent. (by volume) of nitrogen. Any change in the

Mean Specific Heat between 20° and 440°.

1904	t_0	$\frac{z}{(\text{Min.})}$.	$\frac{m}{(g)}$	Θ_1	Θ_2	ϑ	τ_1	τ_2	k	ϑ'	c
					Nitrogen.						
Aug. 24.	18.3°	4	22.90	441.8°	19.4°	4.951°	0.1084°	0.0755°	0.441°	4.510°	0.2403
	18.3	4	22.53	442.1	25.1	4.659	0.0720	0.0385	0.249	4.410	0.2419
Sept. 12.	18.1	3	21.44	444.5	18.9	4.650	0.1105	0.0665	0.332	4.318	0.2438
	18.2	3	21.49	444.7	24.5	4.458	0.0751	0.0413	0.216	4.242	0.2421
	18.0	4	24.62	444.8	18.8	5.376	0.1120	0.0718	0.439	4.937	0.2426
	18.0	4	24.73	444.8	25.0	5.080	0.0702	0.0284	0.226	4.854	0.2409
					Air.						
July 4.	18.1	4	22.44	443.0	18.9	4.821	0.1136	0.0764	0.456	4.365	0.2363
	18.1	4	22.56	444.2	24.6	4.668	0.0757	0.0458	0.289	4.379	0.2384
	18.0	4	21.44	443.4	18.7	4.615	0.1120	0.0766	0.454	4.161	0.2355
	18.0	4	21.61	444.2	24.1	4.471	0.0760	0.0472	0.294	4.177	0.2371
Aug. 24.	18.2	4	22.64	441.7	18.6	4.858	0.1104	0.0784	0.456	4.402	0.2368
	18.2	4	23.74	442.2	24.4	4.828	0.0772	0.0420	0.298	4.530	0.2354
					Oxygen (with 9.5 Per Cent. N.).						
Sept. 12.	18.0	4	25.08	444.4	18.7	5.115	0.1119	0.0741	0.446	4.669	0.2253
	18.0	4	25.63	444.2	24.6	4.935	0.0727	0.0341	0.238	4.697	0.2250
	18.0	3	22.24	445.2	19.2	4.480	0.1094	0.0716	0.343	4.137	0.2250
	18.0	3	22.84	445.3	23.8	4.421	0.0715	0.0313	0.185	4.236	0.2267
					Carbon Dioxide.						
Sept. 10.	17.9	3	28.28	442.8	19.1	5.712	0.1113	0.0679	0.337	5.375	0.2312
	17.9	4	26.31	442.8	25.4	5.124	0.0674	0.0219	0.201	4.923	0.2310
	18.0	4	25.00	443.6	19.2	5.139	0.1092	0.0703	0.429	4.710	0.2287
	18.0	3	28.29	441.7	25.2	5.457	0.0695	0.0250	0.167	5.290	0.2313
	18.0	4	29.57	442.8	19.3	6.006	0.1129	0.0678	0.429	5.577	0.2295
	18.1	4	32.54	441.7	26.2	6.228	0.0672	0.0160	0.182	6.046	0.2310

Mean Specific Heat between 20° *and* 630°.

1904	t_0	$\frac{\theta}{(\text{Min.})}$.	$\frac{m}{(g)}$	Θ_1	Θ_2	ϑ	τ_1	τ_2	k	ϑ'	c
						Nitrogen.					
Aug. 25.	18.1°	4	21.27	636.0°	21.4°	6.897°	0.1603°	0.1110°	0.654°	6.243°	0.2461
	18.1	4	21.21	638.4	21.0	6.884	0.1637	0.1141	0.668	6.216	0.2446
	18.0	4	19.72	637.4	21.0	6.456	0.1606	0.1145	0.665	5.791	0.2455
Sept. 14.	18.0	3	18.01	630.4	19.9	5.848	0.1640	0.1163	0.537	5.311	0.2489
	18.0	4	24.72	630.1	22.0	7.791	0.1584	0.0957	0.604	7.187	0.2464
	18.0	4	22.05	630.0	20.6	7.089	0.1612	0.1092	0.650	6.439	0.2469
	18.0	4	21.19	629.8	21.1	6.786	0.1563	0.1066	0.632	6.154	0.2459
	18.0	3	18.74	629.9	20.2	5.997	0.1595	0.1157	0.528	5.469	0.2467
						Air.					
Sept. 15.	18.0	4	21.89	630.7	20.7	6.917	0.1638	0.1088	0.634	6.283	0.2425
	18.0	4	22.29	630.1	21.4	7.018	0.1585	0.1034	0.627	6.391	0.2427
	18.1	3	18.80	628.8	20.2	5.956	0.1641	0.1171	0.539	5.417	0.2440
	18.2	3	19.04	627.4	20.8	5.966	0.1609	0.1150	0.529	5.437	0.2426
	18.2	4	23.96	624.0	21.0	7.472	0.1635	0.1040	0.639	6.833	0.2437
" 19.	18.0	4	22.29	630.2	20.5	7.055	0.1674	0.1130	0.674	6.381	0.2419
						Oxygen (with 9.5 Per Cent. N.).					
Sept. 19.	18.2	3	19.64	634.7	20.1	5.975	0.1677	0.1206	0.553	5.422	0.2315
	18.0	4	23.25	632.9	21.1	7.053	0.1630	0.1094	0.654	6.399	0.2318
	18.0	4	23.65	631.3	21.0	7.109	0.1635	0.1077	0.650	6.459	0.2306
	18.0	3	19.72	633.3	20.8	5.958	0.1604	0.1147	0.527	5.431	0.2317
						Carbon Dioxide.					
Sept. 13.	18.0	3	23.17	630.0	21.8	7.163	0.1573	0.0989	0.483	6.680	0.2443
	18.1	3	23.60	630.0	21.8	7.261	0.1572	0.1000	0.486	6.775	0.2432
	18.0	4	27.67	629.8	22.1	8.472	0.1593	0.0923	0.595	7.877	0.2414
	18.0	4	24.99	629.9	21.7	7.717	0.1578	0.0960	0.604	7.113	0.2412
	18.0	4	20.62	630.0	20.6	6.530	0.1593	0.1096	0.647	5.883	0.2413

Mean Specific Heat between 20° *and* 800°.

1904	t_0	z (Min.).	m (g)	Θ_1	Θ_2	ϑ	τ_1	τ_2	k	ϑ'	c
					Nitrogen.						
Aug. 26.	18.0°	4	19.55	804.3°	22.6°	8.310°	0.2201°	0.1551°	0.905°	7.405°	0.2497
	18.0	4	18.72	800.3	22.8	7.988	0.2169	0.1559	0.901	7.087	0.2509
	18.0	4	20.04	799.5	22.4	8.480	0.2178	0.1539	0.897	7.583	0.2509
Sept. 1.	18.0	4	19.63	801.8	22.8	8.319	0.2230	0.1624	0.933	7.386	0.2489
	18.0	4	18.69	800.8	21.8	8.016	0.2247	0.1649	0.944	7.072	0.2503
" 3.	18.0	4	18.77	798.2	22.0	7.944	0.2218	0.1543	0.940	7.004	0.2477
	18.0	4	18.90	797.6	22.4	7.985	0.2199	0.1508	0.892	7.093	0.2495
					Air.						
Aug. 16.	20.2	4	19.62	797.7	23.1	8.099	0.2241	0.1630	0.937	7.162	0.2428
	20.0	4	17.79	797.3	23.2	7.380	0.2180	0.1620	0.922	6.458	0.2426
	20.0	4	19.80	793.0	22.7	8.171	0.2244	0.1618	0.934	7.237	0.2436
	20.0	3	15.06	796.8	22.6	6.262	0.2201	0.1691	0.753	5.509	0.2435
" 17.	20.2	3	17.01	798.1	23.4	6.979	0.2203	0.1651	0.743	6.236	0.2439
	20.0	4	18.14	796.3	22.4	7.578	0.2245	0.1672	0.95	6.627	0.2433
	20.0	5	18.96	796.1	23.3	7.973	0.2203	0.1592	1.109	6.864	0.2414
					Carbon Dioxide.						
Sept. 1.	17.9	4	20.09	794.0	21.7	8.430	0.2264	0.1613	0.937	7.493	0.2489
	18.0	4	19.62	794.4	22.3	8.212	0.2220	0.1575	0.914	7.298	0.2483
" 3.	18.0	4	19.11	791.6	21.8	8.016	0.2230	0.1556	0.913	7.103	0.2488
	18.0	4	19.29	791.3	22.5	8.018	0.2191	0.1506	0.890	7.128	0.2477
" 5.	18.0	3	19.79	793.5	23.0	8.127	0.2172	0.1505	0.712	7.415	0.2506
	18.1	3	20.97	792.7	22.5	8.568	0.2235	0.1524	0.716	7.852	0.2505
	18.0	4	18.41	791.1	21.9	7.764	0.2230	0.1597	0.957	7.807	0.2477
	18.0	6	20.43	784.3	22.2	8.780	0.2226	0.1545	1.286	7.494	0.2480
	18.0	5	20.32	786.9	22.1	8.563	0.2224	0.1541	1.129	7.434	0.2466

composition of the gas during the experiment by the formation of oxides in the heating tube must be negligible since the passage was so rapid. This was proven by the fact that a specimen of gas sent through rather slowly at 630° showed an increase of less than 1 per cent. of nitrogen. One bomb of nitrogen used contained 1.2 per cent. and the other 5 per cent. oxygen.

Results.

Simple Gases. — The following table shows the mean of the observed values for the mean specific heat of the simple gases.

	Nitrogen.	Oxygen with 9.5 Per Cent. N.	Oxygen.	Air.	Air Calculated from N and O.
Between 20° and 440°	0.2419	0.2255	0.2240	0.2366	0.2377
Between 20° and 630°	0.2464	0.2314	0.2300	0.2429	0.2426
Between 20° and 800°	0.2497	—	—	0.2430	—

The value for pure oxygen was calculated according to the known percentage of nitrogen mixed with it. In the same way a value was calculated for air, derived from the two values for nitrogen and oxygen.

In regard to the specific heat of air between 20° and 440° the difference between our values and those of the earlier observers up to 100° or 200° (Regnault 0.2375, E. Wiedmann 0.2389) lies within the limits of the errors of observation.

Oxygen was investigated by Regnault up to 200°. Two determinations gave for the mean specific heat 0.2163 and 0.2188 giving as an average 0.2175 which is 3.5 per cent. smaller than the value observed by us at 440°. According to this it appears that the specific heat of oxygen increased between 200° and 400°. For comparison we have also made observations on the specific heats of the different gases between 20° and 245°. In this region however, our apparatus was not fitted for absolute measurements. We have therefore merely determined the values relatively, taking air as the normal gas and assuming the Regnault value 0.2375 to be correct.

The results were as follows:

Nitrogen	0.2401
Oxygen with 9.5 per cent. nitrogen	0.2223
Carbon dioxide	0.2197

From this we calculated the value for pure oxygen to be 0.2206 which is still somewhat higher than Regnault found. It is to be observed, however, that these values were derived from observations with comparatively slow gas velocity and very possibly were too small in comparison with the value of air 0.2375 which was found with a powerful gas flow.

So far as we are aware, nitrogen has up to the present never been directly investigated. The value given by Regnault 0.2438 was calculated from his values for air and oxygen.

In regard to the variation of the specific heat with the temperature, it would appear that between 20° and 400°, and 20° and 800° the mean values for nitrogen and air show an increase of 3 per cent. When we consider, however, the variation in the two gases at the same temperature with changes in the condition of the apparatus, and consider further, that the difficulties in determining the temperature of the gas before it enters the calorimeter increase with increasing temperature, it is hardly possible to conclude with certainty from these small changes in the values that the specific heat increases with the temperature. We must therefore at present consider the observed result as merely a limiting value.

Assuming, however, that the variation between 0° and 800° corresponds to the observed values and is linear, and making use of Regnault's values between 10° and 200° we will have the following formula for the mean specific heat c between 0° and θ°

$$c = c_0(1 + 0.00004\theta).$$

where c_0 is the value at 0° and θ the temperature.

Mallard and Le Chatelier as well as Langen have obtained concordant values for the mean specific heat c_v at constant volume at high temperatures by means of explosion experiments. The latter gives for the molecular heat C_v of the simple gases the expression

$$C_v = 4.8 + 0.0006\,\theta$$

for the temperature interval 1300° to 1700°. Assuming that the relation between the molecular heats at constant pressure and constant volume

$$C - C_v = 1.98$$

holds for the whole interval, it follows that the mean specific heat at constant pressure

$$c = c_0 (1 + 0.00008_5 \theta).$$

From our observation it appears that this equation is not applicable to lower temperatures but that here the specific heat increases more slowly.

Carbon Dioxide. — The variation in the specific heat of carbon dioxide is of especial interest, since according to the observations of Regnault and E. Wiedemann there is a well marked increase in its specific heat even at lower temperatures. The following table contains the values of the mean specific heats observed by us. The value for the interval 20° to 200° is taken from earlier observations. In the column Cal. the values given are derived from the formula

$$c = 0.2028 + 0.0000692\theta - 0.00000001167\theta^2.$$

	Obs.	Cal.
Between 20° and 200°	(0.2168)	0.2173
" 20 " 440	0.2306	0.2312
" 20 " 630	0.2423	0.2410
" 20 " 800	0.2486	0.2486

The true specific heat γ_θ at the temperature θ is

$$\gamma_\theta = 0.2028 + 0.0001384\theta - 0.00000005\theta^2$$

while Regnault from his observations in the interval − 30° to + 210° derived the formula

$$\gamma_\theta = 0.1784 + 0.0002918(\theta + 30°) - 0.0000001074(\theta + 30°)^2.$$

Our investigation therefore shows that the specific heat at higher temperatures increases more slowly than an exterpolation of the Regnault formula would indicate.

We give in the next table the values for the true specific heat as calculated from the different formulæ. It is to be observed that these values on account of their derivation from the integral values at the limits of the observed intervals are to a considerable extent uncertain.

At	Regnault.	E. Wiedemann	Mallard and Le Chatelier.	Langen.	Holborn and Austin.
0°	0.1870	0.1952	0.188_0	0.198_0	0.2028
100	0.2145	0.2169	0.214_0	0.210_0	0.2161
200	0.2396	0.2387	0.239_0	0.222_0	0.2285
400			0.284_0	0.245_0	0.2502
600			0.323_0	0.269_0	0.2678
800			0.355_0	0.292_0	0.2815

The values of Mallard and Le Chatelier correspond to the equation

$$C_v = 6.3 + 0.006\theta - 0.0000011 8\theta^2.$$

This equation for the mean molecular heat was derived by these investigators from their explosion experiments and from the observations of Regnault and E. Wiedemann. This formula gives considerably larger values than ours which more nearly correspond to Langen's linear equation

$$C_v = 6.7 + 0.0026\theta.$$

If we calculate the mean specific heat at constant pressure between 0° and 1500°, first according to our formula and then according to that of Langen, we get the values 0.269 and 0.287 which differ from each other by 6 per cent.

Since the two ranges of observation lie far apart from each other it will be necessary to postpone definite conclusions until calorimetric measurements are extended to still higher temperatures.

THE QUADRANT ELECTROMETER, AS USED FOR MEASURING CURRENT.

By O. M. Stewart.

THE extensive use of the quadrant electrometer in radio-activity work justifies some mathematical investigation of the properties of this instrument. Since this use is usually limited to the measurement of small currents through some gas, the following discussion is restricted to this particular work.

In measuring current, the needle of the electrometer is usually charged to a relatively high potential, one pair of quadrants is grounded and the other pair is connected to the conductor into which the current from the gas passes. The observer then determines the rate of motion of the electrometer needle and this is taken to be proportional to the current. That is, in ordinary use one assumes that

$$\frac{d\theta}{dt} = k_1 i$$

where θ is the angular deflection of the needle, i the current through the ionized gas and k_1 a constant. The elementary proof of this is sometimes given as follows:

Let C be the capacity of the pair of quadrants and the apparatus connected to it, Q the charge on it and V_1 its potential. Then

$$Q = CV_1. \tag{1}$$

By differentiating, we have

$$\frac{dQ}{dt} = C\frac{dV_1}{dt} = i. \tag{2}$$

If V_2 is the potential of the needle we have

$$\theta = k_2 V_1 V_2, \tag{3}$$

where k_2 is a constant.

Then,

$$\frac{d\theta}{dt} = k_2 V_2 \frac{dV_1}{dt}. \tag{4}$$

By comparing (2) and (4) one finds that $d\theta/dt$ is proportional to the current i.

This involves two assumptions; first, that the capacity is a constant and second that equation (3) which holds for steady deflections is true when the needle is in motion. Equation (3) follows from a statement of the equilibrium existing between the electrostatic forces which tend to deflect the needle and the torsional force of the suspension which tends to restore the needle to its zero. This equation is not true when the needle is in motion, for in that case there is another force introduced, the damping. Even for a uniformly increasing potential and a uniform velocity of the needle, equation (3) does not hold, for due to this force of damping which tends to assist the torsional force of the suspension, the deflection is always less than for the steady deflection.

The capacity of the electrometer changes as the needle moves; but if the capacity of the apparatus connected to the electrometer is large this change may be neglected. However, in many instances this cannot be neglected. Professor Thomson[1] has shown that when a needle moves there is a certain effective capacity which for a given potential of the needle is a constant. He has, however, assumed equation (3) which as we have just seen is not correct when θ is varying. But this equation has been used in such a way that as will be shown later his results are correct when the velocity of the needle has become constant. That is, the effective capacity is a constant when the needle is moving without acceleration. This will be discussed more in detail later. For the present we will assume that the capacity is constant, that is, the special case where the capacity of the apparatus is large compared to that of the electrometer.

If we assume a constant capacity and wish to measure a steady current i we have, from (2),

$$i = C\frac{dV_1}{dt},$$

[1] Philosophical Magazine, 46, p. 537, 1898.

and by integration

$$V_1 = \frac{i}{C}t,$$

where V_1 is the varying potential of one pair of quadrants. The moment of force tending to deflect the needle is at any instant equal to

$$kV_1V_2,$$

when the potential of the needle, V_2, is large compared to V_1. Hence the moment of force is given by

$$\frac{ki}{C}V_2t = Et. \tag{5}$$

Since the factors of the coefficient of t are here assumed constant E is a constant. E may be said to be the time rate of change of the electrostatic torque on the needle.

The general equation of the motion of the needle may then be written,

$$A\frac{d^2\theta}{dt^2} + B\frac{d\theta}{dt} + D\theta = Et, \tag{6}$$

where A is the moment of inertia of the needle, B the damping factor and D is the moment of torsion of the fiber.

The complementary solution of this equation is obtained by equating the left hand member to zero and solving.

$$A\frac{d^2\theta}{dt^2} + B\frac{d\theta}{dt} + D\theta = 0. \tag{7}$$

The solution of (7) is

$$\theta = Me^{(\alpha+\gamma)t} + Ne^{(\alpha-\gamma)t}, \tag{8}$$

where

$$\alpha = -\frac{B}{2A}$$

and

$$\gamma = \sqrt{\frac{B^2}{4A^2} - \frac{D}{A}}.$$

The particular solution of (6) is

$$\theta = \frac{E}{D}\left(t - \frac{B}{D}\right). \tag{9}$$

Hence the complete solution is

$$\theta = Me^{(\alpha+\gamma)t} + Ne^{(\alpha-\gamma)t} + \frac{E}{D}\left(t - \frac{B}{D}\right). \tag{10}$$

In this solution, γ may be real or imaginary. Equation (10) will therefore reduce to one of two types, depending on the relation between the damping on the one hand and the moments of inertia and torsion on the other. There is also the special case where $\gamma = 0$.

γ *real.*

In this case

$$B^2 > 4\,AD.$$

When the time t is zero we know that

$$\theta = 0, \text{ and } \frac{d\theta}{dt} = 0.$$

Applying these initial conditions to equation (10) and solving for the constants M and N, one obtains

$$M = -\frac{E}{2D\gamma}\left(1 + (\alpha - \gamma)\frac{B}{D}\right),$$

$$N = \frac{E}{2D\gamma}\left(1 + (\alpha + \gamma)\frac{B}{D}\right).$$

Substituting these in (10),

$$\theta = \frac{E}{D}\left\{\frac{1}{2\gamma}e^{(\alpha-\gamma)t}\left(1 + (\alpha+\gamma)\frac{B}{D}\right)\right.$$

$$\left. - \frac{1}{2\gamma}e^{(\alpha+\gamma)t}\left(1+(\alpha-\gamma)\frac{B}{D}\right) + t - \frac{B}{D}\right\} \tag{11}$$

From this by differentiating and remembering that $\alpha = -B/2A$ and that $\alpha^2 - \gamma^2 = D/A$, the value of the angular velocity is

$$\frac{d\theta}{dt} = \frac{E}{D}\left(1 - \frac{\kappa+\gamma}{2\gamma}\, e^{-(\kappa-\gamma)t} + \frac{\kappa-\gamma}{2\gamma}\, e^{-(\kappa+\gamma)t}\right). \qquad (12)$$

For convenience κ has been written for $-\alpha$. When t is large

$$\frac{d\theta}{dt} = \frac{E}{D}$$

Hence the angular velocity approaches a constant value which depends only on E and D the moment of torsion.

γ zero.

Equation (10) is not a complete solution of (6) when γ is zero for it then contains only one constant. The form of the solution of (7) may be taken as

$$\theta = e^{\alpha t}(R + St)$$

and the complete solution of (6) as

$$\theta = e^{-\frac{B}{2A}t}(R + st) + \frac{E}{D}\left(t - \frac{B}{D}\right).$$

Putting in the initial conditions one has for the displacement,

$$\theta = e^{-\frac{B}{2A}t}\left(\frac{BE}{D^2} + \frac{E}{D}t\right) + \frac{E}{D}\left(t - \frac{B}{D}\right)$$

or

$$\theta = \frac{E}{D}\left[e^{-\frac{B}{2A}t}\left(\frac{B}{D} + t\right) + t - \frac{B}{D}\right]. \qquad (13)$$

The angular velocity becomes on differentiating

$$\frac{d\theta}{dt} = \frac{E}{D}\left[1 - e^{-\frac{B}{2A}t}\left(1 + \frac{B}{2A}t\right)\right],$$

since $B^2 = 4AD$ when $\gamma = 0$.

Writing κ for $B/2A$ this becomes,

$$\frac{d\theta}{dt} = \frac{E}{D}[1 - e^{-\kappa t}(1 + \kappa t)]. \qquad (14)$$

In this case also the angular velocity $d\theta/dt$ becomes practically equal to E/D after some time.

γ imaginary.

Let $\gamma = i\beta$ where $i = \sqrt{-1}$
Then

$$\beta^2 = \frac{D}{A} - \frac{B^2}{4A^2}.$$

The solution of equation (7) is now

$$\theta = e^{\alpha t}(M' \cos \beta t + N' \sin \beta t)$$

and the complete solution of (6) is

$$\theta = e^{\alpha t}(M' \cos \beta t + N' \sin \beta t) + \frac{E}{D}\left(t - \frac{B}{D}\right). \qquad (15)$$

Applying the initial conditions

$$\theta = 0 \text{ and } \frac{d\theta}{dt} = 0,$$

and substituting the values of M' and thus N' obtained in (15) we have

$$\theta = \frac{E}{D}\left[\frac{B}{D}e^{\alpha t}\cos \beta t - \frac{1}{\beta}\left(\frac{\alpha B}{D} + 1\right)e^{\alpha t} \sin \beta t + t - \frac{B}{D}\right]. \qquad (16)$$

Differentiating this and remembering that $\alpha^2 + \beta^2 = D/A$, the expression for the angular velocity is obtained

$$\frac{d\theta}{dt} = \frac{E}{D}\left[1 - e^{-\kappa t}\left(\cos \beta t + \frac{\kappa}{\beta} \sin \beta t\right)\right], \qquad (17)$$

as before κ has been written for $-\alpha$.

In this case the velocity approaches the final velocity E/D with a damped periodic motion. The period of this motion is given by

$$\tau = \frac{2\pi}{\beta}.$$

By solving (17) for maximum and minimum values of the velocity, it may be shown that the velocity reaches a maximum at $t = \tau/2$, a minimum at $t = \tau$, with another maximum at $t = 3\tau/2$ and so on.

The velocities at these times are given by the following equations: When,

$$t = \frac{\tau}{2}, \qquad \frac{d\theta}{dt} = \frac{E}{D}\left(1 + e^{\frac{-\kappa\tau}{2}}\right),$$

$$t = \tau, \qquad \frac{d\theta}{dt} = \frac{E}{D}\left(1 - e^{-\kappa\tau}\right),$$

$$t = \frac{3}{2}\tau \qquad \frac{d\theta}{dt} = \frac{E}{D}\left(1 - e^{\frac{-3\kappa\tau}{2}}\right),$$

In curve 1, on p. 238, is shown the relation between the angular velocity and the time. The data for this curve was obtained from equation (17) by substituting in it the constants of a particular instrument. The angular velocities are plotted relatively, the final velocity E/D being taken as unity.

Hence in all cases as is shown by equations (12), (14) and (17), the final velocity is given by

$$\frac{d\theta}{dt} = \frac{E}{D}.$$

That is, the final velocity depends only on E, the rate of change of the electro-static torque acting on the needle and D the moment of torsion of the suspension.

Substituting the value of E from equation (5) in the above value of $d\theta/dt$ we have

$$\frac{d\theta}{dt} = \frac{kiV_2}{CD}. \tag{18}$$

But kV_2/D is the constant k' of the electrometer in the equation

$$\theta = k' V_1.$$

The final uniform velocity is therefore proportional to the current whose value is sought. If the capacity C is known, then i can be at once determined. It may be noted that the final velocity is independent of the moment of inertia of the needle and B the damping coefficient.

The important question that arises in every case is, — How long is it until the needle reaches this final velocity? Considerable light

may be thrown on this by considering another motion of the needle. Let the free pair of quadrants be raised to any convenient potential and the steady deflection θ_0 noted. If the quadrants are now grounded, the needle will return to its zero position. The equation of its motion in this case is given by

$$A\frac{d^2\theta}{dt} + B\frac{d\theta}{dt} + D\theta = 0.$$

The complete solution of this is

$$\theta = Me^{(\alpha+\gamma)t} + Ne^{(\alpha-\gamma)t}, \tag{19}$$

where as before, $\alpha = -B/2A$ and $\gamma^2 = B^2/4A^2 - D/A$. As before three cases arise, γ real, imaginary, and equal to zero. In each case we have the initial conditions,

$$\theta = \theta_0, \quad \frac{d\theta}{dt} = 0.$$

When γ is real, equation (19) becomes, on substituting for M and N the values found by these initial conditions,

$$\theta = \theta_0\left(\frac{\kappa+\gamma}{2\gamma}\, e^{-(\kappa+\gamma)t} - \frac{\kappa-\gamma}{2\gamma}\, e^{-(\kappa+\gamma)t}\right), \tag{20}$$

or the motion is aperiodic. As before κ has been written for $-\alpha$. When γ is imaginary (19) becomes

$$\theta = e^{-\kappa t}(M\cos i\beta t + N\sin i\beta t). \tag{21}$$

Solving again for M and N by applying the initial conditions and inserting these values in (21) one obtains

$$\theta = \theta_0 e^{-\kappa t}\left(\cos i\beta t + \frac{\kappa}{i\beta}\sin i\beta t\right). \tag{22}$$

In this case the needle swings through the zero and the period of its vibration is given by

$$\tau = \frac{2\pi}{i\beta}.$$

Proceeding in a similar way for the case $\gamma = 0$ one obtains

$$\theta = \theta_0 e^{-\kappa t}(1+\kappa). \tag{23}$$

In the equations (20), (22) and (23) the quantities κ, γ and β are the same as before.

The terms that contain the coefficients of the exponentials in equations (12), (14), (17) are identical with the corresponding terms in equations (20), (23) and (21). Hence we find a general rule *that the velocity approaches its final value at the same rate and in the same manner that the deflected needle when released by grounding the quadrants, returns to its zero.* For example, suppose that the needle of a particular instrument had been displaced a scale distance of 20 cm. and then released. It was noted that 25 seconds elapsed before the needle was within 1 cm. of its zero, or 5 per cent. of the initial deflection. Then if this instrument were used to measure a constant current, it would be 25 seconds from the time of insulating the quadrants until the velocity of the needle had come within 95 per cent. of the final value.

The maximum values of θ in (22) occur when, $t = 0$, $t = \tau$, $t = 2\tau$, etc. Or when

$$\begin{aligned} t &= 0, \quad \theta_1 = \theta_0, \\ t &= \tau, \quad \theta_2 = \theta_0 e^{-\kappa\tau}, \\ t &= 2\tau, \quad \theta_3 = \theta_0 e^{-2\kappa\tau}. \end{aligned}$$

From this it is seen that,

$$\log_e \frac{\theta_1}{\theta_2} = \kappa\tau.$$

Or $\kappa\tau$ is the "logarithmic decrement." Since τ can be observed, κ may be computed. Thus, from the observations on the decay of a vibration the constants, κ and β, of the equation (17) can be computed. In this way the period and logarithmic decrement of a sensitive electrometer of the Dolezalek type[1] were observed. Curve I. shown in the figure was plotted by substituting these values in equation (17). In this instrument only air damping is used. As is shown by this curve it is necessary to wait about 30 seconds before the velocity becomes approximately constant. It is of some practical interest to know what can be gained by changing the constants of the instrument to shorten this time. With this electrometer observation gave

[1] Made by Cambridge Instrument Co.

$$\tau = 24 \text{ seconds}$$

and the mean ratio of consecutive throws 22.6. Hence

$$\log_e 22.6 = 3.12 = \kappa\tau.$$

Or

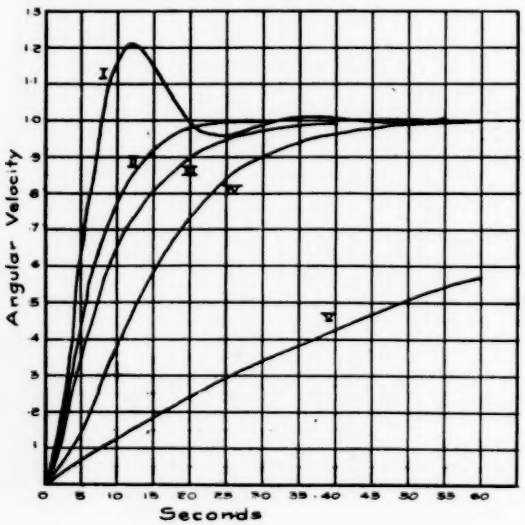
$$\kappa = .13.$$

But since,

$$\frac{D}{A} - \kappa^2 = \beta^2 = \frac{4\pi^2}{\tau^2} = .68,$$

$$\frac{D}{A} = .085.$$

If κ^2 be increased to .085, that is if κ be increased from 0.13 to 0.29 β becomes zero and the motion aperiodic. Curve II. was com-



puted from equation (14) by using this changed value of κ. It is seen from this curve that there is a distinct gain in increasing the damping.

If the damping be increased beyond this critical value, the velocity will approach its final constant value more slowly. Curve III. is the result obtained when the damping factor is increased about 35 per cent. of the value used in the case of Curve II., all the other quantities

remaining unchanged. Curve V. shows the effect of increasing the damping ten fold. Both of these curves are computed from equation (12). It is apparent that too much damping is to be avoided. In adjusting the damping, use can be made of the rule just given, that is by noting how soon the needle returns to zero after being deflected.

If instead of changing the damping a more delicate fiber be used the motion may become aperiodic, for D is decreased and D/A may become less than κ^2. However the undamped period is increased and in general the time for the velocity to reach an approximately constant value is not decreased. Curve IV. was plotted from equation (14) by assuming that D had been decreased until the motion just became aperiodic. D would have to be reduced to one fifth its original value. While there has been in this way a decided gain in sensibility, a considerably longer time is required for the needle to reach a uniform speed.

Capacity not Constant.

In the preceding work it has been assumed that the capacity of the electrometer as compared to that of the rest of the apparatus was so small that the change in it could be neglected. We shall now consider the more general case, that where the change in the capacity of the quadrants is taken into account.

If V_1 is the potential of one pair of quadrants, V_3 that of the other and V_2 that of the needle we have, Q_1 being the charge on the first pair of quadrants,

$$Q_1 = q_{11}V_1 + q_{12}V_2 + q_{13}V_3, \qquad (24)$$

where q_{11}, q_{12}, q_{13} are coefficients of capacity. q_{11} is the charge on 1 when V_1 is unity and all others are grounded; q_{12} is the charge on 1 when V_2 is unity and all others are grounded, and so for q_{13}. We shall consider that one pair of quadrants is always grounded, that is that $V_3 = 0$. When the needle moves both q_{11} and q_{12} change. If the needle is approximately symmetrically placed with respect to the quadrants and θ is not large, one may assume the change in q_{12} is proportional to the deflection, or that

$$\frac{dq_{12}}{d\theta} = a,$$

a constant. With this assumption it has been shown,[1] that

$$q_{12} = C_{12} + a\theta,$$

$$q_{11} = C_{11} - a\theta,$$

where C_{12} and C_{11} are the values of q_{12} and q_{11} when θ is zero. Substituting these values in equation (24) and remembering that V_3 is always zero, we have

$$Q_1 = C_{11}V_1 + C_{12}V_2 + a\theta(V_2 - V_1) \tag{25}$$

The potential of the needle, V_2, is large compared to V_1, hence we may neglect V_1 in the last term. Solving (25) for V_1,

$$V_1 = \frac{1}{C_{11}}(Q_1 - C_{12}V_2 - a\theta V_2). \tag{26}$$

But the electrostatic moment of force tending to deflect the needle is

$$kV_1V_2.$$

Substituting in this the above values of V_1 we have for the value of the moment,

$$\frac{kV_2}{C_1}(Q_1 - C_{12}V_2 - a\theta V_2). \tag{27}$$

$C_{12}V_2$ is quantity of electricity induced on the quadrants when V_1 and θ are zero, and the increase due to a current i is

$$Q_1 - C_{12}V_2 = it.$$

Substituting this we have for the deflecting moment

$$\frac{kV_2}{C_{11}}(it - a\theta V_2). \tag{28}$$

The equation of motion then becomes

$$A\frac{d^2\theta}{dt^2} + B\frac{d\theta}{dt} + D\theta = \frac{kV_2}{C_{11}}(it - a\theta V_2),$$

[1] Maxwell, "Electricity and Magnetism," Vol. I., Art. 219; Thomson, Phil. Mag., 46, p. 537, 1898.

or

$$A\frac{d^2\theta}{dt^2} + B\frac{d\theta}{dt} + \left(D + \frac{akV_2^2}{C_{11}}\right)\theta = \frac{kV_2^2}{C_{11}}t. \qquad (29)$$

This may be written

$$A\frac{d^2\theta}{dt^2} + B\frac{d\theta}{dt} + D'\theta = Et. \qquad (30)$$

The coefficient of θ is the only quantity in this equation that differs from equation (6). Hence it appears that the effect of this increase of capacity is mechanically the same as an increase in the moment of torsion of the suspension. There is this difference that while the change in the capacity is continuous, the equivalent change in the moment of torsion is an absolute change. The capacity C_{11} includes the capacity of the apparatus connected to the free quadrants

The value of the velocity obtained from (30) is

$$\frac{d\theta}{dt} = \frac{E}{D'}\left[1 - e^{-\kappa t}\left(\cos \beta' t + \frac{\kappa}{\beta'}\sin \beta' t\right)\right], \qquad (31)$$

where

$$\beta' = \frac{D'}{A} - \frac{B^2}{4A^2}.$$

As D' is larger than D, β' is larger than β and the periodic time is shortened. Since κ is not changed and the period less, the needle will reach the approximately uniform velocity sooner.

The solution in the aperiodic case is

$$\frac{d\theta}{dt} = \frac{E}{D'}\left[1 - \frac{\kappa + \gamma'}{2\gamma'}e^{-(\kappa - \gamma')t} + \frac{\kappa - \gamma'}{2\gamma'}e^{-(\kappa + \gamma')t}\right], \qquad (32)$$

where

$$\gamma'^2 = \frac{B^2}{4A^2} - \frac{D'}{A}.$$

Owing to the increase of D', γ' is less than γ. The second term on the right hand side of (32) is larger than the last and is therefore, so far as the decay is concerned, the more important term. This term is decreased by the decrease in γ. Hence the time for the velocity to reach an approximately uniform velocity is shortened. This increase in D tends to make an aperiodic motion become peri-

odic, but even in this case will not tend to increase the time for the acquirement of a practically uniform velocity.

When the velocity becomes uniform, in each case,

$$\frac{d\theta}{dt} = \frac{E}{D'} = \frac{kiV_2}{D\left(C_{11} + \frac{k}{D} a V_2^2\right)}. \tag{33}$$

Here, as in the case where the capacity was regarded as a constant, the velocity is proportioned to the current. In the case where the capacity was uniform it was shown that the simple method of noting the time for the needle to return to approximate rest at its zero point gives the time for the velocity to become approximately constant. When the change of capacity is appreciable, this time is shortened. This method, however, gives a safe limit for the beginning of observations.

On comparing equation (33) to equation (18) it is seen that the quantity

$$C_{11} + \frac{k}{D} a V^2$$

corresponds to the capacity C in that equation. It has been called the effective capacity and the value as here found is identical to that found by Professor Thomson. This quantity, however, is the effective capacity only when the velocity of the needle has become uniform.[1] It is this capacity that one measures when the divided charge method is employed and the change in the deflection of the electrometer itself is used.[2]

If k' be defined by the equation

$$\theta = k' V_1 V_2,$$

where θ is the steady deflection,

$$k' = \frac{k}{D}$$

[1] Strictly speaking, it is the effective capacity when there is no acceleration. It is the effective capacity when the needle is moving with uniform speed and also when the needle is allowed to come to rest as in the method of measuring charges or capacities.

[2] For example, the method given in Rutherford's "Radioactivity," p. 86.

The effective capacity[1] may then be written

$$C_{11} + k' a V_2^2.$$

An inspection of equation (33) shows that as the potential of the needle is increased the velocity $d\theta/dt$ goes through a maximum value. This maximum value is reached, as shown by differentiating (33) and equating to zero, when

$$C_{11} = \frac{k}{D} a V_2^2 = k' a V_2^2. \tag{34}$$

The maximum sensibility for current work as the potential of the needle is increased, is therefore reached when the effective capacity is twice the capacity in the case where the needle is kept at zero This however assumes that k' is constant. It is well known that k changes when the potential of the needle becomes large, so that the sensibility as indicated by steady deflections passes a maximum as V_2 is increased. If however the capacity of the apparatus connected to the electrometer is small, it may happen that the potential of the needle is above the maximum value of current sensibility yet well within the maximum for ordinary sensibility. The sensibility for current measurement however does not change much with the change of the potential of the needle, so that there is no practical gain in adjusting the needle potential to this maximum.

Equation (33) may be written

$$\frac{d\theta}{dt} = \frac{kiV_2}{DC_{11} + kaV_2^2}.$$

The only quantity in this equation affected by changing the suspension is D the moment of torsion of the suspension. It is obvious that while the sensibility of the electrometer for a steady deflection is inversely proportional to D, the sensibility for current measurements is not effected as much by changes in D.

[1] It may be shown, see Maxwell, l. c., that

$$a = k,$$

hence the effective capacity may be written

$$C_{11} + k' k V^2.$$

The ratio between the change of the capacity of the electrometer due to the motion of the needle and the capacity when the needle is stationary can be found experimentally by a simple method. Starting with the quadrants earthed, one pair is insulated and then connected for an instant only to some source having a potential V_1. If this pair has been insulated before the needle moves an appreciable amount, the needle will swing around to a deflection θ_1. If however connection to the potential V_1 is maintained until the needle comes to rest, a deflection θ_2 is observed. The ratio of this last deflection to the other is the ratio of the effective capacity to the capacity when the needle does not move. Another method is to let the needle take a deflection θ corresponding to the potential V of the free quadrant. This pair of quadrants is now insulated and then grounded for an instant. The needle will not return to zero but will take a deflection θ_1. The ratio of the deflection θ to θ_1 is equal to the ratio of the effective capacity to the difference between the effective capacity and that when the needle is not free to move. Both of these statements are readily proven. If the potential of the other pair of quadrants is always zero and the needle is charged to a potential high compared to that used on the quadrants, equation (25) may be written

$$Q_1 = C_{11}V_1 + C_{12}V_2 + a\theta V_2.$$

If in the first case θ be zero and a potential V_1 be applied we have

$$Q_1 = C_{11}V_1 + C_{12}V_2.$$

When the needle moves Q_1 remains constant and V_1 changes to V'. The needle will come to rest at θ_1 and

$$Q_1 = C_{11}V' + C_{12}V_2 + a\theta_1 V_2$$

where θ_1 is the deflection corresponding to a potential V'.

Equating the two left handed members we have

$$C_{11}V_1 = C_{11}V' + a\theta_1 V_2.$$

But

$$\theta_1 = k'V'V_2,$$

$$\therefore C_{11}V_1 = (C_{11} + k'V_2^2)V',$$

$$\therefore \frac{V_1}{V_2} = \frac{C_{11} + ak' V_2^2}{C_{11}} = \frac{\theta_2}{\theta_1}.$$

Or

$$\frac{ak' V_2^2}{C_{11}} = \frac{\theta_2}{\theta_1} - 1.$$

It may be shown in a similar manner that in the second case

$$\frac{C_{11} + ak' V_2^2}{ak' V_2^2} = \frac{\theta}{\theta_1},$$

or

$$\frac{C_{11}}{k' V_2^2} = \frac{\theta}{\theta_1} - 1.$$

These methods assume that the period of the needle is large enough so that a contact can be made and broken before the needle moves an appreciable amount. If large deflections are used, errors due to the small charge given by contact effects at the make and break point are not important. Moreover, if the same metal is used for both surfaces of the contact key, as for example, two clean pieces of copper wire, the disturbing effect will be insignificant.

A trial with the electrometer, from which curves shown in Fig. 1 were deduced, gave by both methods the ratio

$$\frac{ak' V_2^2}{C_{11}} = 2.0.$$

V_2 was in this case about 100 volts. With this potential of the needle the electrometer gave about 600 mm. deflection on a scale 1 meter distant for a difference of potential of one volt.

By using one of these methods with and without the rest of the apparatus connected to the electrometer one can compare the capacity of the whole to that of the electrometer itself.

There is a method available for comparing currents in which one does not need to wait until the velocity has become uniform. The method is to observe the deflection reached in a given time after the quadrants are insulated. If the same time interval is used in all the observations, the deflection in each case will be proportional to the current. This can be seen by an inspection of the equations (11), (13) and (16). Since A, B and D, and therefore α, β and γ are

constants, θ is proportional to E if a constant value of t is used. But E, see equation (5), is proportional to the current i. This is also true in the general case where the capacity is not a constant. For in this case the effect is to change D to D', see equation (30), and D' is a constant. This method is of great advantage where the readings must be taken quickly. It has the disadvantage that with sensitive electrometers the break of the earth connection often imparts a slight initial charge to the quadrants. The equations (11) (13) and (16) show that the deflection for a given value of t is not proportional to the sensibility of the instrument. For example the sensibility varies inversely with D, yet this deflection according to these equations will not vary inversely as D. This method has the additional disadvantage, that the absolute value of the current can not readily be computed, as in the case where one waits until the velocity has become uniform.

The method of comparing or determining the current by observing the time required for the needle to move a certain amount does not give correct results unless the needle is moving with a uniform velocity.

STUDIES OF LUMINESCENCE.

By Edward L. Nichols and Ernest Merritt.

V. The Luminescence of Sidot Blende.[1]

AMONG the substances whose luminescence is sufficiently bright for spectrophotometric study Sidot blende, or phosphorescent zinc sulphide, seems especially well suited to bring out the relationships that doubtless exist between different types of luminescence; for not only is this substance excited to luminescence by all known exciting agents — light, Roentgen rays, radium rays, cathode rays, etc. — but the stimulating effect of heat, and the property possessed by the red and infra-red rays of suppressing phosphorescence, are exhibited in unusual degree. It is for this reason that we have chosen this substance for spectrophotometric study. While it is our intention to extend this study to all of the various types of luminescence whose quantitative investigation is practicable, the present communication deals only with luminescence excited by light and by Roentgen rays.

The material used in these experiments was in the form of a screen, of the kind frequently used in exhibiting the properties of radium and for numerous experiments in which it is desirable to have a fluorescent substance in convenient form. The experimental methods were similar to those employed in our previous work on fluorescence, a Lummer-Brodhun spectrophotometer, with an acetylene flame as a comparison source, being used to measure the intensity in different parts of the luminescence spectrum. In certain portions of the work special devices were required which will be described in their proper place.

Luminescence Excited by Roentgen Rays.

The screen was placed in front of the collimator slit of the spectrophotometer at a distance of only a few centimeters, while the

[1] An account of the experiments described in this paper was presented to the American Physical Society at the Philadelphia meeting December 30, 1904. An abstract appeared in the Physical Review vol. 20, p. 120, 1905.

Queen self regulating tube used for excitation was about twenty centimeters behind the screen. Roentgen rays of moderate "hardness" were used. No systematic experiments to determine the effect of varying hardness upon the form of the luminescence spectrum have yet been made, but a few preliminary tests indicate that the effect is not great. Corrections due to fluorescence excited in the glass of the spectrophotometer, which we had at first thought would be necessary, were found to be negligible.

The upper curve in Fig. 30 shows the luminescence spectrum observed during excitation, while the lower curve shows the distribution of intensity in the phosphorescence spectrum, observed 5 sec. after excitation had ceased. Owing to the weakness of the phosphorescence excited by Roentgen rays, the latter curve was determined with some difficulty, the readings at the red end of the spectrum being especially uncertain. The indications of a second maximum in the phosphorescence spectrum at 0.62 μ or beyond are therefore not to be regarded as entirely trustworthy.

PHOTO-LUMINESCENCE DURING EXCITATION.

In the experiments upon photo-luminescence during excitation the carbon arc was first used as an exciting source. The arrangement of apparatus is shown in Fig. 31. The zinc sulphide screen was

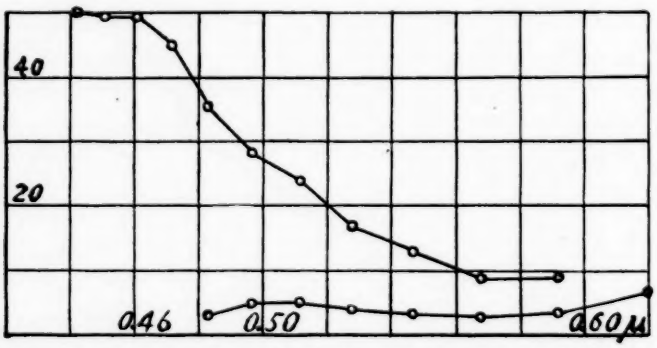


Fig. 30. The upper curve shows the luminescence spectrum of Sidot blende during excitation by Roentgen rays. The lower curve shows the phosphorescence 5 seconds after excitation.

placed in a light tight box B, and the exciting light from an arc A, after dispersion by the pris m P, entered the box through an open

ing at the left. A second opening in B allowed the fluorescence light to enter the slit of the Lummer-Brodhun spectrophotometer S_1. The comparison source was an acetylene flame F whose rays were reflected into the comparison slit by the block of magnesium carbonate, M. The second spectrophotometer, S_2, and the shutter C were used in later experiments on phosphorescence, but not in the experiments now considered.

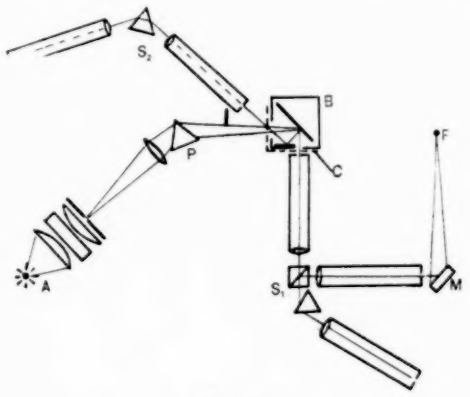


Fig. 31.

Luminescence was excited only by the rays at the violet end of the arc spectrum, and especially in the region of the violet bands. It is to be noted that on account of the absorption of the glass prism and lenses the spectrum extended only a short distance into the ultra violet.

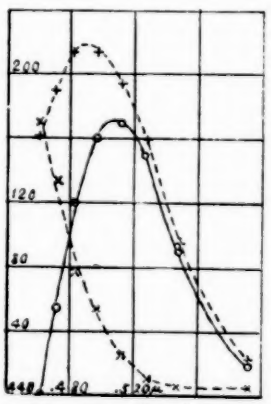


Fig. 32. Luminescence spectrum of Sidot blende during excitation by the violet bands in the arc.

Observations taken to determine the luminescence spectrum when the zinc sulphide screen was excited by the violet bands of the arc are plotted in Fig. 32. Owing to the impurity of the exciting spectrum a certain amount of blue and green light reached the screen even when the attempt was made to excite by violet only. Since this stray light was in part reflected into the slit of the spectrophometer with the luminescence light of the same color, it was necessary to make a correction to remove the error due to this cause. The correction was determined by replacing the zinc sulphide screen by a block of magnesium carbonate, whose surface was of approximately the same color and roughness as that of the fluorescent screen, and by measuring the light received from the magnesia

at different points throughout the spectrum. The results of such a series of measurements is shown in the lower broken line in the figure. It will be noticed that the correction is inappreciable for the longer wave-lengths, but becomes important in the violet. The upper broken line in Fig. 32 shows the intensity of the light reaching the spectrophotometer from the zinc sulphide screen, being the combined effect of luminescence and reflected light; and the heavy curve, obtained by subtracting the ordinates of the lower curve from those of the upper, shows the corrected luminescence spectrum during excitation.

The curves in Fig. 32, like those published in our previous papers on luminescence, are expressed in terms of the acetylene flame as a standard. In other words, each ordinate represents the ratio of the intensity of the luminescence light, of the particular wave-length considered, to the intensity of the light of the same wave-length from an acetylene flame; the curves are not energy curves. Since, however, the distribution of energy in the visible spectrum of the acetylene flame is now known,[1] curves showing the energy distribution in luminescence spectra may readily be computed if desired.

When the screen was excited by the arc as described above no trace of the violet luminescence, which had been so prominent with Roentgen ray excitation, could be observed. It seemed not unlikely, however, that the absence of the violet band was due to the fact that the ultraviolet rays suitable for exciting it had been removed from the light from the arc by the glass prism and lenses of the dispersing system. We therefore rearranged the apparatus so as to use a quartz prism and quartz lenses, while a spark between metal terminals was substituted for the arc. Since the excitation in the region studied was solely by ultraviolet rays that were incapable of passing through glass, it was a simple matter to test for errors due an impure spectrum, or to any other source of stray light, by inserting a piece of glass in the path of the exciting rays. This test showed that stray light was in no case present in appreciable amount.

[1] Nichols, Standards of Light, Proc. International Electrical Congress at St. Louis, 1904. PHYSICAL REVIEW, vol. XXI., p. 147, 1905.

This ultraviolet excitation developed strong fluorescence in the extreme violet, similar in color to that produced by Roentgen rays. But the green band that had been excited by the visible rays of the arc was relatively very weak. In spite of its faintness, however, the presence of the green band in the luminescence light could be readily detected, for while the violet luminescence died out almost immediately when excitation ceased, the green persisted as a slowly decaying phósphorescence observable for several minutes.

The similarity between the effects of ultraviolet light and those of Roentgen rays as exciting sources is worthy of note. In each case the chief luminescence is in the extreme violet, and is of short duration. But in each case also this is accompanied by luminescence in the green, which is relatively faint but of long duration. As is illustrated in numerous other cases, the Roentgen rays, when comparable at all with rays of light, are rather to be compared with ultraviolet light than with the rays of the visible spectrum.

The agreement between the luminescence spectrum excited by Roentgen rays and that observed in the case of ultraviolet excitation is not exact. We are of the opinion that the difference is due

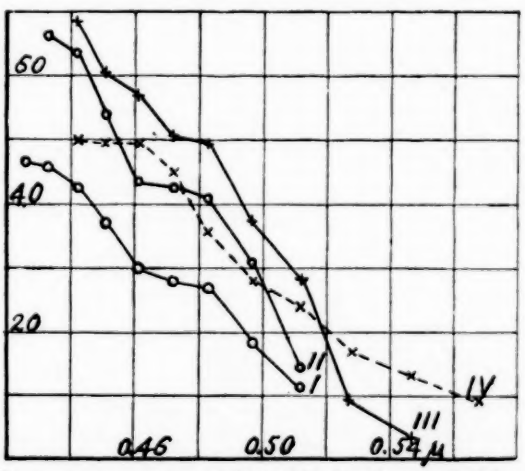


Fig. 33. Fluorescence spectrum of Sidot blende when excited by the ultra-violet rays of the iron spark (Curves I. and II.), by the ultra-violet of the magnesium spark (Curve III.), and by the Roentgen Rays (Curve IV.).

to the fact that the violet luminescence does not consist of one band only, but of at least two, which are excited by Roentgen rays and

ultraviolet light in different relative intensity. The matter will be made clear by reference to Fig. 33. Curve I. shows the luminescence spectrum when ultraviolet rays from the iron spark were used for excitation. The rays used were those giving most intense luminescence, and did not lie much beyond the edge of the visible spectrum. The shape of this curve suggests that it is made up of two overlapping bands, one having a maximum not far from 0.48 μ, while the other has its maximum near 0.42 μ. In Curve II. the exciting light was at the extreme ultra end of the iron spectrum, and in Curve III. the magnesium lines near 0.33 μ were used in excitation. In these curves also there is every indication that the spectrum consists of at least two bands.

Unfortunately we have not been able to separate the bands more completely. It is to be remembered that the resolving power of a spectrophotometer is at the best small, and that in experiments of the kind here described the small intensity of the light studied prohibits the use of a narrow slit. Luminescence bands may sometimes be separated by a proper choice of the exciting light. In the case of Sidot blende the green band is very readily obtained alone by using the carbon bands of the arc for excitation. But the two violet bands in the luminescence of this substance are so close together that their regions of excitation appear to overlap throughout nearly their whole extent. The most that we were able to do was to show that ultraviolet rays of different wave-length produced different relative intensities in the two bands, as illustrated by Curves I. and III. of Fig. 33.

The broken line, Curve IV. of Fig. 33 shows the luminescence spectrum excited by Roentgen rays. This is the same curve that appears in Fig. 30, and is introduced in Fig. 33 to make possible convenient comparison of the effects of ultraviolet light and Roentgen rays. It will be observed that each of the curves in Fig. 33 might well result from the superposition of three bands, whose maxima lie approximately at 0.42 μ, 0.48 μ and 0.51 μ. In the Roentgen ray luminescence the green band is relatively stronger than in the case of excitation by ultra-violet light, while the band at 0.48 μ appears to be entirely absent. In the luminescence produced by the magnesium spark (Curve III.) the green band, while still observable, is not so

strong as in Curve IV., while the band at 0.48 μ is readily detected. Curves I. and II. (iron spark) show scarcely any trace of the green band, but the bands at 0.48 μ and at 0.42 μ are well marked.

Failure of Stokes' Law.

As already stated, the green band is most brilliantly excited by the violet, although rays from all parts of the ultraviolet spectrum are also capable of producing a considerable effect. We thus see that there is the same general relation between the position of the luminescence spectrum and that of the exciting light as in the case of fluorescence. In all the cases of fluorescence thus far studied we have found that the two spectral regions overlap. It therefore seemed interesting to see whether the same is true in the present case.

To settle this point it was necessary to use in excitation a far purer spectrum than that employed in our other experiments with Sidot blende. The rather crude dispersing system shown in Fig. 31 was therefore replaced by a large spectrometer. A spectrum of the arc was thrown on the collimator slit by the aid of a prism and single lens, and after a second dispersion in the spectrometer, light reached the phosphorescent screen as a sharply focussed band. Using the shutter described below so as to observe the phosphorescence immediately after the exciting light was cut off, and making observations with the unaided eye instead of with the spectrophotometer, it was found that phosphorescence was unquestionably present for exciting light lying between 0.470 μ and 0.497 μ. Since the phosphorescence spectrum can readily be followed beyond 0.46 μ there appears to be the same violation of Stokes' law in the phosphorescence of Sidot blende that we have previously found in the case of fluorescence.

Phosphorescence Spectrum During Decadence.

Although the phosphorescence of Sidot blende can be detected in a dark room for several hours after excitation has ceased, it remains sufficiently bright for spectrophotometric measurement only for a few seconds. In order to determine the law of decay for different

wave-lengths and especially to determine the change, if any, in the phosphorescence spectrum during decay, the following procedure was followed:

A shutter, shown by the broken line C in Fig. 31, and sliding upon vertical guides, was attached to the box containing the phosphorescent screen. When this shutter was raised it permitted the exciting light to enter the box, as in the experiments just described, but at the same time closed the opening in front of the collimator slit. When the shutter was dropped it first cut off the exciting light and then, a moment later, opened the window in front of the collimator. The observer was in this way protected from the brilliant luminescence produced during excitation, but was enabled to observe the phosphorescence immediately after excitation had ceased. The comparison slit being set to some suitable reading, the observer recorded upon a chronograph the instant when the two parts of the spectrophotometer field appeared equally bright. By means of a suitable electric contact on the shutter a record was also made at the time when the exciting light was cut off. In this way the time required for the phosphorescent light to fall from its initial value to any given final value could be conveniently measured.

The determination of the instant when the rapidly changing phosphorescence became equal to the constant comparison light would at first appear to be a difficult observation, and one not capable of great accuracy. As a matter of fact these observations were fully as reliable as ordinary spectrophotometric settings, and at these low intensities far less trying to the eye.

The most serious difficulty encountered in these measurements arose from the unsteadiness of the exciting light. When constancy is essential the arc, even under the best of conditions, leaves much to be desired. After numerous unsuccessful attempts to obtain steady conditions we abandoned all special efforts to keep the excitation constant, and arranged to make observations only when the exciting light, either by adjustment or by accidental fluctuation, had reached a certain definite intensity. In order to accomplish this a second spectrophotometer (S_2 in Fig. 31) was used. Light from the luminescent screen was thrown into the collimator by means of a mirror as shown in the figure. The comparison light came

from the acetylene flame F after reflection from a mirror and a block of magnesium carbonate not shown in the figure. One observer at the eyepiece of S_2 waited until the intensity of fluorescence reached such a value as to give equality of the two fields, and then, with suitable warning, dropped the shutter C. The second observer at S_1 then made a chronograph record as before described. Numerous determinations, often twenty or more, were made in this way for each point of the curves described below.

A preliminary set of measurements in which the duration of excitation was varied from 3 sec. to 30 sec. showed no variation in the time of decay. We conclude that the full effect of the exciting light is produced in less than 3 sec. In the subsequent experiment the duration of excitation was never less than 5 sec.

TABLE I.

Giving the observed time, in seconds, during which the phosphorescence fell from its initial intensity to the intensity given at the top of the column.

Wave-length.	$I = 100$.	$I = 60$.	$I = 0$.	$I = 10$.	$I = 5$.
0.461 μ				0.458	
0.472		0.00		0.99	
0.483	0.00	0.456	0.745	2.07	7.1
0.497	0.491	0.95	1.63	3.13	
0.512	0.502	1.00	1.80	3.41	10.4
0.528	0.290	0.682	1.49	2.91	
0.535	0.00				
0.547		0.223	0.838	2.55	7.5
0.553		0.00			
0.568			0.302	1.30	
0.572			0.00		
0.592				0.713	4.1

The results of one set of determinations made in this way are given in Table I. and are plotted in Fig. 34. In Curve I. the width of the comparison slit was kept at 100 divisions of its micrometer screw, and the time required for the phosphorescence of any given wave-length to fall from its initial value to this intensity was determined as described above. The curve is obtained by plotting wave-lengths as abscissas and times as ordinates. In Curve II. the width of the comparison slit was 60 divisions; in Curve III., 30 divisions; and in Curve IV., 10 divisions. Obser-

vations made at 5 divisions are not included on the plot. Points lying on the horizontal axis in Fig. 34 were located by determining

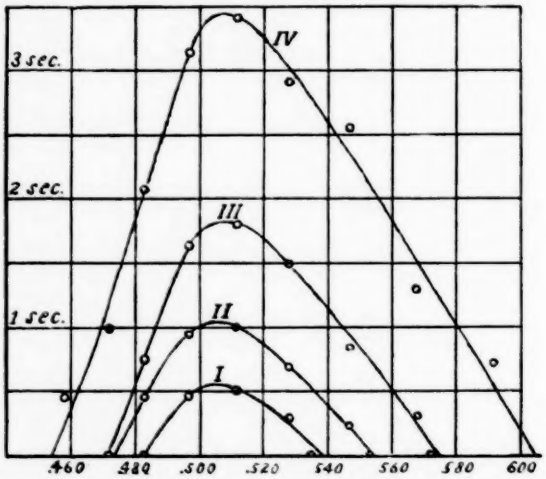


Fig. 34. Curves showing the time required for the phosphorescence to fall from its initial intensity to a given final intensity. The final intensity is kept constant throughout each curve.

by trial the wave-length for which there was a balance in the spectrophotometer the instant after dropping the shutter. These points are probably somewhat less reliable than the others.

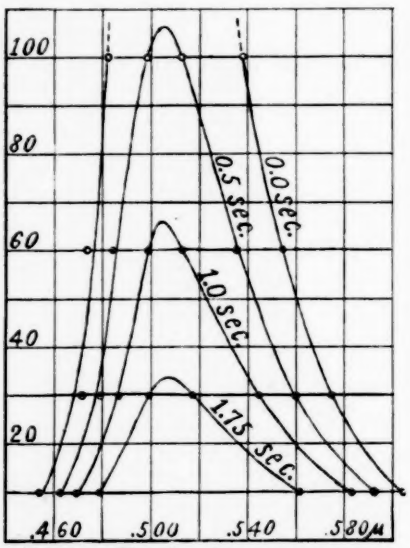


Fig. 35. The phosphorescence spectrum of Sidot blende at different times after the removal of the exciting light.

The significance of these results is better shown by plotting them in a different way. In Fig. 35 wave-lengths are plotted as abscissas as before, but intensities, instead of times, are plotted as ordinates. Each curve in this figure shows the distribution of intensity in the phosphorescence spectrum at some definite time after the removal of the exciting light.

No curves have been plotted for intervals of more than

1.75 sec. after excitation had ceased, since our data furnished so few points for the later curves that their form would be largely a matter of conjecture.[1] As already stated, however, a curve of the type shown in Fig. 34 was determined for an intensity of 5 divisions. The maximum ordinate of this curve was 10.1 sec. and occurred at 0.506 μ — *i. e.*, at the same wave-length as in the case of the curves shown in 34. Comparison with Fig. 32 shows that the maximum of the luminescence spectrum during excitation also occurs at this wave-length. In the case of the green band of Sidot blende we conclude therefore that the maximum of the fluorescence spectrum occurs at the same wave-length as that of the phosphorescence spectrum; and that no change that could be detected by our apparatus occurs in the position of this maximum for ten seconds after excitation has ceased.

Fig. 35 also shows that if any change occurs in the form of the phosphorescence spectrum during decadence, this change is extremely small. In other words the different wave-lengths of the phosphorescent spectrum decay at the same rate. Table II. will show to what extent this conclusion is justified by the data. Each column of this table refers to the wave-length stated at the top, and in it are tabulated the intensities for this wave-length at different intervals after the end of excitation, these intensities being expressed in terms of the intensity at the end of 1.75 sec. as unity. If the phosphorescence spectrum remains absolutely unaltered during decay, all the numbers in this table that lie in a given horizontal line should be equal.

TABLE II.

Intensity of Phosphorescence at Different Intervals After Excitation Had Ceased, Expressed in Terms of the Intensity at the End of 1.75 *Sec.*

	0.48 μ	0.50 μ	0.52 μ	0.54 μ	0.56 μ
0.0 sec.	7.8 ?			5.2	4.8
0.5 "	3.5	3.3	3.1	3.0	2.8
1.0 "	1.9	2.0	1.8	1.8	1.9
1.75 "	1.0	1.0	1.0	1.0	1.0

[1] In a series of observations of the kind recorded in Fig. 34 the number of points that could be located was limited both by the difficulty of maintaining constant conditions during the three or four hours of observation, and by the endurance of the observer's eye.

The numbers in Table II. corresponding to 0.0 sec. are uncertain; first, because the observations by which the initial phosphorescence was determined were themselves especially uncertain; and second, because the steepness of the curve (Fig. 35) in the neighborhood of 0.48 μ and 0.54 μ would cause a slight change in the manner of plotting to produce a large change in the ordinates at these wave-lengths. If the ratios tabulated for 0.0 sec. are left out of consideration, the agreement between the remaining ratios, at 0.5 sec. and 1.0 sec. is as close as could be expected. We conclude that, although there is some indication of more rapid decadence at the ultra edge of the phosphorescence spectrum, the probability is that all parts of the spectrum decay at the same rate, and that the form of the phosphorescence spectrum remained unchanged.

While the result obtained in this one case is not sufficient to establish a general law, we are nevertheless of the opinion that the behavior of Sidot blende is typical, and that in no case of phosphorescence is there any change in the form of the spectrum during decadence. In complex cases of phosphorescence we do not imply by this that the phosphorescence spectrum as a whole remains unchanged in form, but rather that the distribution of intensity in each band is unaltered. If the phosphorescence consists of several bands, it is to be expected that the different bands will decay at different rates. In fact Sidot blende itself furnishes an extreme illustration of this, for the violet bands die out in one or two tenths of a second, while the green band persists for hours.

Numerous cases in which the color of a phosphorescent substance seems to change as the phosphorescence dies out at first appear to contradict this view absolutely. We think, however, that all cases of this kind may be shown to belong to one of the two following classes:

1. Cases of real color change. For example, anisic acid at low temperatures, where the phosphorescence changes from blue to greenish yellow.[1] Such cases are probably due to the presence in the luminescence spectrum of several phosphorescence bands, which decay at different rates. In the case of anisic acid the results would be explained by the presence of a brilliant but rapidly decaying

[1] Nichols and Merritt, PHYSICAL REVIEW, vol. 18, p. 355, 1904.

band in the blue, and a persistent band of smaller initial intensity in the yellow.

2. Cases where the apparent change in color is due to the fact that the color sense in the eye is either weak or entirely absent at low intensities. At very low intensities all colors appear to the eye as gray. However brilliant may be the color of the phosphorescence light initially, it loses this color and changes to a gray or faint white as it becomes fainter. But such a change as this is in the retina, and does not indicate any change in the phosphorescence spectrum. We are convinced that the use of the unaided eye in the study of luminescence may lead to serious errors.

It is interesting to note that attention was called to both of these causes of change of color during decay by the elder Becquerel.[1]

The data of Table I. might also be used to study the law of decay of phosphorescence, *i. e.*, the relation between intensity and time. More reliable results are obtained, however, by studying one wave-length at a time, since the data necessary for plotting a decadence curve may in this case be obtained more quickly and are, therefore, less liable to error due to fluctuating conditions. Experiments dealing with the law of decadence and with the effect of infra-red radiation upon phosphorescence will be described later.

[1] Ed. Becquerel, C. R., vol. 49, p. 27, 1859; Ann. de Chemie et de Physique. Series 4, vol. 62, p. 20, 1861.

THE JOULE-THOMSON EFFECT IN CARBON-DIOXIDE. I. EXPERIMENTAL.

BY FREDERICK E. KESTER.

HISTORICAL SUMMARY.

THE original Joule experiments, the aim of which was the determination of the amount of work done against the forces of intermolecular attraction when a gas expands without doing external work, were performed in 1844.[1] The apparatus, used by him, consisted of two copper flasks, each of about 2.2 liters capacity, joined by a pipe and a stop-cock, which opened or closed the connection between them; the whole was submerged in a water calorimeter. The air having been removed from one of the flasks by pumping to a very low pressure and the test gas having been pumped into the other to a high pressure, it is evident that, upon opening the stop-cock, the expansion of the gas to twice its original volume, took place without the performance of external work. Any fall or rise in the temperature of the gas as a whole must have meant a decrease or an increase in the kinetic energy of its molecular motions with an equal increase or decrease in the potential energy of molecular separation. But, in spite of the facts that initial pressures as high as 22 atm. were used and that the calorimeter was so shaped that the water used was reduced to the smallest allowable amount, no noticeable change in the temperature of the bath occurred. It must be regretted that this apparatus cannot be made sensitive enough to measure the amount of energy changed from one form into the other during the expansion, for here the effect sought is a pure one — no part of the internal energy is expended in external work — an advantage which no other form of apparatus possesses.

It was during a report by Joule, upon these experiments, before the Royal Society in 1844, that Thomson became interested in the

[1] J. P. Joule, Phil. Mag. (3), **26**, 369, 1845; Joule's Scientific Papers, I., 172.

problem ; to him is due the porous plug form of apparatus. With it the method employed is to maintain constant gas pressures on the two sides of a plug of porous material, packed tightly into a short length of the gas path. The flow through the plug is then a steady one, of such character that practically no work is done in giving the gas a kinetic energy due to an increase in its stream velocity — the flow is a diffusion process. Here, however, the thermal effect obtained is no longer a pure one ; the difference in the temperatures of the gas before it enters and after it leaves the plug is due both to the work done against molecular attractions and to the difference between the values of the product $p \cdot v$ (p = pressure ; v = specific volume) which exist on the two sides of the plug. This difference is the difference between the amount of work done upon one gram of the gas in forcing it into the porous plug and the amount done by one gram of the gas as it leaves the plug. The product $p \cdot v$ will have different values on the two sides of the plug, not only because the particular gas in use does not follow Boyle's law ; the difference in temperature, caused by the change in the potential energy of the molecules, will of itself establish a difference between the values of the product. Just how large a fraction of the total thermal effect this external factor may become in special cases will be shown later in a discussion of experimental results. I speak of it here at some length in order to make as clear as possible the errors which are liable to affect any theoretical discussion involving (implicitly or explicitly) a separation of the total observed thermal effect into its component parts ; although the whole may have been measured with considerable accuracy, it may not be possible to make this separation with the same nicety.

The series of researches carried on by Joule and Thomson,[1] with the porous-plug form of apparatus, extended through the years from 1852 to 1862, and included work on air, oxygen, nitrogen, carbon dioxide, hydrogen and mixtures of two or more of these.

Following the same principle which underlies the porous-plug experiment, Hirn [2] made a series of observations upon the cooling

[1] Joule and Thomson, Phil. Mag. (4), **4**, 481, 1852 ; Phil. Trans., **143**, 357, 1853 ; Phil. Trans., **144**, 321, 1854 ; Phil, Trans., **152**, 579, 1862 ; Joule's Sci. Pap., II., 216 ; Kelvin's Math. and Phys. Pap., I., 333.

[2] G. A. Hirn, Théorie Mech. de la chaleur (3 éd.), II., 387.

effect experienced by steam (in both the saturated and superheated states) when it expands from various pressures to atmospheric pressure. The expansion in these experiments did not take place through a porous-plug, but through a small opening into a large, well-jacketed space; in order to destroy (partially at least) the high stream velocity resulting from the free expansion, the steam was made to impinge upon a flat surface placed only a short distance in front of the opening through which it expanded.

Then, returning to the original form of apparatus used by Joule — that of the double flask — Cazin[1] performed a number of experiments upon air, carbon dioxide and hydrogen. In his work, although the form of apparatus was essentially the same as Joule's, the method of experiment was very different and much more complicated. In its main features the method was as follows: With the large stop-cock between the flasks open, the pressure of the contained gas was measured by suitable manometers, and the temperature, brought to the same value in the two chambers, was observed. The stop-cock was closed, a *part* of the gas was pumped from one flask into the other and the flasks and contained gas were brought to the original temperature, under which conditions the new pressures were measured. Then with the stop-cock wide open, the gas was allowed to expand suddenly from the one flask into the other; as soon as the pressures had become equal the cock was closed, and a series of pressure and time readings were taken while the temperatures were brought again to the original value. Finally the stop-cock was opened, the temperatures were brought a fourth time to the same original value and the common pressure was measured. By this last step any loss of gas, which may have occurred during the pumping or expansion, could have been detected. The pressure and time readings were used to indicate the value of the common pressure at the time of opening the stop-cock; the knowledge of this pressure completed the data, from which the state of the gas at each step was determined. The whole process could then be subjected to thermo-dynamic analysis. The relation between this method of procedure and that of Joule's will be readily understood by observing that Cazin measured (implicitly)

[1] A. Cazin; Ann. de Chim. et de Phys. (4), **19**, 5. 1870.

the changes in temperature of the gas by means of the pressure changes. On account of numerous complications the results of these experiments are open to serious criticism, and in the later discussion of the results of the various researches they will not be considered.

From the time of Cazin's work no other experimental results upon this problem appeared until those of Natanson[1] were published in 1887. His work was done with the porous-plug form of apparatus, the same in all important features as that of Joule and Thomson. Natanson's observations were made upon only one gas, CO_2, and at room temperature. The method of procedure was to keep the difference of the pressures on the two sides of the plug very nearly the same (about one atmosphere) in all of his experiments and to vary the initial pressure of the gas at will, whereas in the Joule-Thomson researches the pressure behind the plug was kept the same (barometric pressure) and the pressure in front varied. The highest pressure used by Natanson was nearly 25 atm., and between the lowest and this highest pressure he found a decided dependence of the cooling effect of CO_2 upon pressure, whereas Joule and Thomson had been unable to detect (up to 6 atm.) any such dependence in the case of any gas. Natanson, in the report on his work, lays special emphasis upon the remarkable purity of the gas used in his experiments, and criticises the Joule-Thomson results on this ground, though the criticism as made is not a fair one.

In 1898 Witkowski[2] published a report on the determination of the cooling effects in air when it was allowed to expand through a series of porous plugs spaced along a considerable length of tube. Nothing but a review of this article has been available in the libraries consulted; consequently no judgment can be given here concerning the value of the results.

More recently a very interesting determination of the inversion temperature of the Joule-Thomson effect in hydrogen was made by Olszewski.[3] The expansion in this case took place through a small

[1] E. Natanson, Wied. Ann., **31**, 502, 1887.

[2] A. W. Witkowski, Rozprawy der Krakauer Akad., math-naturw. Klasse, **35**, 282, 1898; Beiblätter, **23**, 411, 1899.

[3] K. Olszewski, Ann. d. Phys., **7**, 818, 1902.

opening into a large space in which the jets and eddies were dissipated into thermal (molecular) motions, as in Hirn's experiments. In the expansion chamber was placed a delicately constructed platinum thermometer coil, and this chamber together with the spiral tube which led the hydrogen to the small jet-opening was submerged in a cooling bath. The temperature of the bath was so adjusted that, after all parts of the apparatus had reached the proper thermal condition and the jet was opened, no change in the resistance of the platinum coil could be detected.

The present research, the results of which are to be described in this paper, was undertaken at the suggestion of Professor Nichols. It was started in the past academic year (1903–4) in Professor Voigt's division of the Physical Laboratory in Göttingen and the results of this preliminary part of the work were published in January of this year.[1] The general arrangement of apparatus, both in Göttingen and in Ithaca, has been in principle the same as that of Joule and Thomson and of Natanson. One essential difference lies in the use of thermo-electric junctions placed in the gas path, instead of thermometers, for the measurement of the temperature changes. Various important alterations, in the present apparatus, from the design and from the method of manipulation of last year will be mentioned below.

I shall express here my sincere thanks for the valuable suggestions and for the kindly encouragement and direction given to me by Professor Nichols and Professor Merritt. I wish also to thank Professor Moler for many suggestions as to the construction of apparatus. Nothing in my work has been more pleasant than the uniformly courteous treatment which I have found throughout the department.

Description of Apparatus.

A general diagram of the apparatus is given in Fig. 1. The gas was obtained in the usual CO_2 cylinders which contain about 20 pounds of liquid CO_2. This quantity is equivalent to 4,500 or 4,600 liters of gas under normal conditions. The great advantages of such a source lies in the high pressures and in the steadiness of the pressure under which the gas is delivered from them: at room tem-

[1] F. E. Kester, Phys. Zeitschr., **6**, 44, 1905.

perature the vapor pressure of CO_2 is 55–60 atm. In order to avoid a great decrease in the temperature of the liquid, due to evaporation, the cylinders were placed in a water bath while in use; this was especially necessary when the determinations were made at high pressures, for then the quantity of gas delivered to the apparatus was very great.

The water vapor, carried along with the gas, was removed by calcium chloride contained in the U-shaped drying tube. Examination of the drying material, when it was thought advisable to inspect the condition of the tube, left no doubt as to the thorough-

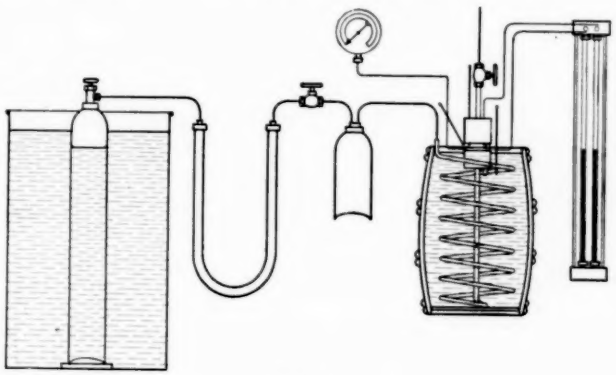


Fig. 1.

ness of its action; the chloride in the last branch of the tube seemed perfectly dry, and was easily shaken out; that in the first branch (at least that in the top part) was somewhat moist; how far down this state of affairs extended could not be discovered for the material could not be shaken out. The tube was washed out, thoroughly dried and refilled with fresh chloride.

The control valve through which the gas next passed is well adapted, by its form of construction, to this use. Its needle is small — about 2.5 mm. in mean diameter — and only slightly conical. The regulation of the pressure in the part of the apparatus beyond it could be made with considerable nicety by means of a short lever arm attached to the hand-grip of the valve.

From the valve, the gas next passed into the small cylinder which served as a pressure equalizing reservoir. Its capacity is 4.3 liters; the volume of this part of the apparatus — from valve to valve — is very nearly 5 liters.

The copper tube, which led the gas from the equalizing chamber up to the porous plug is 10 mm. in inner diameter, 1.25 mm. in wall thickness and about 8 m. long. Before it was wound into spiral form its complete length was threaded with long, spiral, steel lathe-turnings. This was done to break up the possible formation of any well defined stream lines, which would prevent the gas from coming thoroughly into contact with the walls of the tube. The mass of water in which the spiral was submerged was about 100 kg.

After passing through the plug the gas escaped through the second needle valve into the open.

The construction of the nozzle, in the middle of which the porous plug is held, is shown in detail by Fig. 2. The same plug was used for all the experiments of this year's work; it contains 3.4 g. of clean cotton fiber, compressed between two thin perforated disks of steel into a space 15 mm. in diameter and 24 mm. in height. The material immediately surrounding it is the red "vulcanized fiber" which is found so useful in electrical construction. It is inferior to hard rubber in heat insulation, but rubber could not be considered for this purpose because it becomes semiplastic long before it reaches the temperature of boiling water. The small tube which holds the upper steel disk in place is also of this same material. The steel cylinder, which surrounds the vulcanized fiber nozzle, is provided with screw caps as shown; lead washers are used in packing the joints. The thermo-electric junctions are made of steel and constantan wires 0.18 mm. in diameter and are carried by plugs of vulcanized fiber. The wires are cemented in place with a mixture of litharge and glycerine — a cement which serves remarkably well for such purposes. The plugs themselves are held hard upon the seats, cut for them in the steel cylinder, by means of steel encircling rings, each of which is provided with a slot on one side and a set screw diametrically opposite. Pressure tubes lead into the gas path at points indicated in the drawing; one is joined to the pressure gauge (see Fig. 1); the others to the mercury pressure-differenee manometer. Finally the two oil cups, one surrounding the lower part of the nozzle, the other the upper part, are held in place as shown. Each of these baths as well as the large water bath is provided with a stirrer; a small motor furnishes power for all of them.

Electrical heating coils were used in the various baths to maintain constant temperatures when determinations were made above room temperature ; ice, in the large water bath, and copper tubes, in the oil baths, through which cold salt-water flowed, were used in the determinations at 0° C.

This part of the apparatus is in design quite different from the nozzle used last year in the preliminary part of this research. The changes were made in order to accomplish (1) observations at higher temperatures than would have been possible of attainment with hard rubber ; (2) the insertion of the thermal junctions into place without the necessity of unsoldering and resoldering after they had been calibrated ; (3) a definite control of temperatures about the two parts of the nozzle.

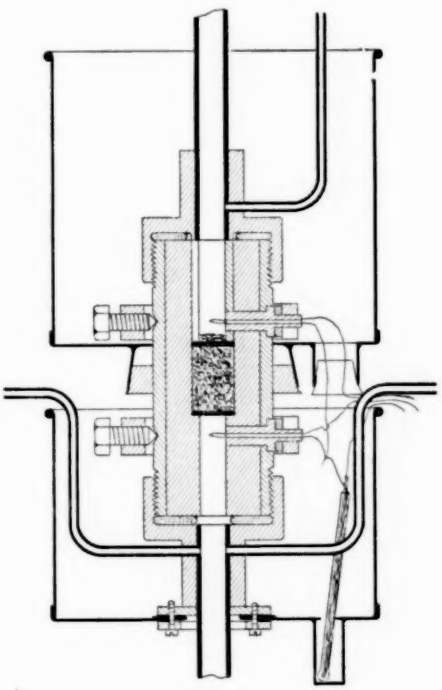


Fig. 2.

The whole apparatus was designed to work up to a pressure of 50 atm. with a factor of safety of at least 2 in all parts. The highest pressure at which determinations were made was 41 atm.

A set of the usual gas analysis pieces was used to determine the amount of impurity in samples of the gas taken from the apparatus after a determination was finished. A solution of KOH was used to absorb the CO_2 and the residue was then measured.

The electrical circuits are shown diagrammatically in Fig. 3. The method involved is that of the potentiometer somewhat modified. The two thermo-electric junctions in the gas path constitute a couple for the measurement of the difference of temperatures above and below the porous-plug ; the junction in the bath and one of the

others serve to measure the difference between the bath temperature and the gas temperature. The steel wires I are brought to a common junction; the constantan wires C are joined one to each of the three wires which lead to the switch S and to the potentiometer wire AB. To avoid, as far as possible, junctions between dissimilar metals all lead wires and the wire AB are of constantan; an important advantage results also from the fact that the resistance of AB remains constant even though the room temperature vary considerably.

The closed circuit, of which the potentiometer wire is a part, consists of a dry cell as a source of current, a variable resistance (part of which is a liquid resistance for fine adjustment of current strength),

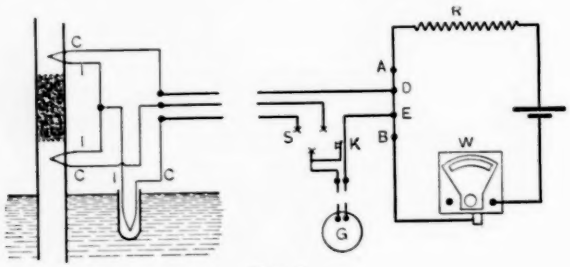


Fig. 3.

the potentiometer wire AB and a Weston voltmeter used as an ammeter. The sensitiveness of this instrument is such that a full scale deflection is caused by a current somewhat less than 0.01 amp. In order to use it in the circuit, a connection is inserted so that the current flows through only the moving coil (of about 70 ohms resist.).

The switch S deserves special notice. In circuits where the electromotive forces are as small as those which are handled here (the greatest value of the e.m.f. in this part of the circuit during observations was about 0.00007 v., and the aim, during the construction of the circuits, was to keep the stray e.m.f.'s within one five-hundredth of this maxim) no ordinary form of switch can be used satisfactorily even when extreme care is taken in the thermal isolation of the working parts. The construction of the switch is shown in Fig. 4; an ordinary three-way glass stop-cock was used for the purpose, and mercury serves as the conducting material.

No description will be necessary to make the drawing clear, unless it be such as will call attention to the precaution of sealing thin-walled glass tubes onto the heavy ones where they entered the mercury jacket. The three constantan wires which lead to the switch enter the tubes from above and dip into the mercury. This use of stop-cocks as electrical commutators and switches is due to des Coudres.[1]

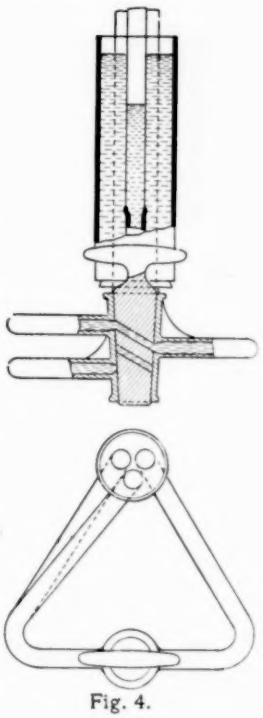


Fig. 4.

The galvanometer G is of the moving coil type, It is the one which was constructed in this laboratory by White and was fully described by him last year in this REVIEW.[2] At all soldered junctions, even where wires of the same metal joined and especially where dissimilar metals joined, precautions were taken to keep corresponding junctions at the same temperature. But in the galvanometer different materials were used in the various parts, and this precaution could not readily be taken. Trouble from this source was avoided by using a piece of constantan wire as a short-circuiting key K. With S open and K closed, a deflection of the galvanometer needle usually occurred; the steady reading of the galvanometer with S and K in these positions was taken as the zero point of the apparatus at the time. A long study of the circuits showed that, with a pair of the steel-constantan junctions submerged in the same bath of mercury as near each other as possible, with no current flowing in the potentiometer wire AB and with S properly closed, the galvanometer deflection never differed from that obtained by opening S and closing K as much as the maximum error, mentioned above, would allow. This method of taking the zero point was, therefore, justified.

[1] Th. des Coudres, Wied. Ann., **43**, 673, 1891.
[2] W. P. White, PHYS. REV., **19**, 305, 904.

CALIBRATION. MANIPULATION. SOURCES OF ERROR.

No great amount of care was necessary in order to measure gas pressures and pressure differences with sufficient accuracy. The observations of last year upon CO_2 at room temperature, showed that the dependence, if any, of the thermal effect upon pressure is so slight that the use of a pressure gauge with even tolerably large scale errors would have been allowable, provided that the mechanism be delicate enough to indicate small changes in pressure. The instrument used in the present apparatus has a range of 1,000 lbs. per sq. in. and a least count of 4 lbs.; motions of the pointer corresponding to pressure changes of 0.5 lb. could readily be detected and slight tappings on the gauge insured a corresponding freedom of motion of the mechanism.

The mercury pressure-difference manometer was read by means of clips which fit nicely to the glass tubes and reach over to a wooden meter bar between the tubes. An error of as much as 1 mm. in the determination of a total height of mercury of 700 or 800 mm. would have been less serious than the errors which could not be avoided in the temperature measurements.

Each of the three baths was provided with a Baudin thermometer of 100° range subdivided to fifths of a degree; readings to fiftieths could easily be made. The stem of each one was calibrated throughout its length and corrections were calculated from this calibration and from determinations of the fixed points. The thermometer in the large bath was always submerged to a point only a little below the top of the mercury thread; therefore no stem correction (due to a difference between the temperature of the stem and that of the bath) was necessary for this one. Auxiliary thermometers were tied to the stems of the other bath thermometers and stem corrections, calculated from the readings of the auxiliaries and from the lengths of mercury threads out of the baths, were applied.

The first step made in the calibration of the electrical part of the apparatus was to check the accuracy of the Weston instrument scale at small intervals. This was done with the aid of a potentiometer. The departures of the ammeter readings from a propor-

tionality to the strengths of current which produced them was in no case greater than 0.2 of a scale division.

In the calibration of the thermal junctions three Baudin thermometers, each of 12° range, subdivided to fiftieths of a degree, and a Golaz thermometer, of similar construction, were used. The Baudin thermometers (0°–13°, 12°–23°, 22°–33°) were sent to the National Bureau of Standards for comparison with the standard thermometers of that institution. After their return to this laboratory the Golaz was carefully compared with the Baudin of 12°–23° range and these two were used in the actual calibration of the working thermal junctions. By means of a magnifying eye-piece, which was made for this purpose, thermometer readings were estimated to 0°.001 ; errors due to jumping of the mercury threads were avoided as far as possible by taking readings while the temperatures were slowly rising.

It was, of course, not to be expected that accuracy such as this could be attained in baths when the temperatures were far from that of the room, and as the junctions were to be used in determinations at temperatures from 0° to 100° some method was necessary by which a careful calibration at room temperature could be extended. This was done by use of an auxiliary thermal couple (the working junctions could not be used on account of the length of wires necessary). One junction of the couple was kept at 0° C. while the other was carried over the range of temperatures from 0° to 100°. For this part of the calibration the potentiometer wire (AB of Fig. 3) was made of such length that the points D and E were 100 cm. apart. The resistance of this length of wire having been measured and the constant of the ammeter being known, it was possible to reduce the ammeter readings to micro-volts. The parabola

$$e = a \cdot t + b \cdot t^2$$

was then fitted to the observations. The third column of the following table gives the e.m.f.'s calculated from this equation with $a = 50.8_4$ and $b = 0.021_9$. The significance of the columns of residuals will be better understood when it is stated that one tenth of an ammeter division is equivalent to about 4 micro-volts of thermo-electromotive force.

Temperature (Degrees).	E.M.F. (Microvolts).		
	Observed.	Calculated.	Residuals.
18.78	965	962	+3
0.08	3.0 (?)	4	−1
2.07	101	105	−4
2.14	102	108	−6
7.23	364	369	−5
7.29	367	372	−5
7.40	375	377	−2
11.77	596	601	−5
11.80	601	603	−2
11.81	601	603	−2
21.27	1,091	1,091	
21.24	1,087	1,089	−2
21.20	1,087	1,087	
26.03	1,337	1,339	−2
25.96	1,336	1,335	+1
25.91	1,335	1,332	+3
31.91	1,644	1,645	−1
31.72	1,635	1,636	−1
31.59	1,625	1,629	−4
99.52	5,276	5,276	

From the above equation we have as the thermo-electric power of this particular steel and constantan

$$de/dt = a + 2bt = 50.8_4 + 0.043_8 \cdot t = 50.8_4(1 + 0.00086_2 \cdot t)$$

The determination of the "temperature coefficient" (0.00086_2) of thermo-electric power of these metals was the aim of this part of the work.

The actual calibration of the working junctions at room temperature was next made. Two mercury baths were used for this purpose; the mercury was contained in two small, cylindrical Dewar bulbs submerged side by side, nearly to their tops in the same bath of water. The thermal junctions were protected with thin coatings of collodion and one was placed in each of the mercury baths close to the bulb of one of the two thermometers mentioned above. The long potentiometer wire was replaced by a short constantan wire 1 mm. in diameter, and DE was made 14 mm. (resistance about 0.009 ohm).

Fig. 5 shows the results of a calibration, made before determinations on the thermal effect had been begun. Only one calibration

was made before the determinations because this one checked so closely two calibrations of a couple, which was broken before it could be used, that more were considered unnecessary. The intention was to make a second calibration after all determinations had been finished, but in removing the junctions from their places, one of the small plugs was broken ; recalibration was therefore impos-

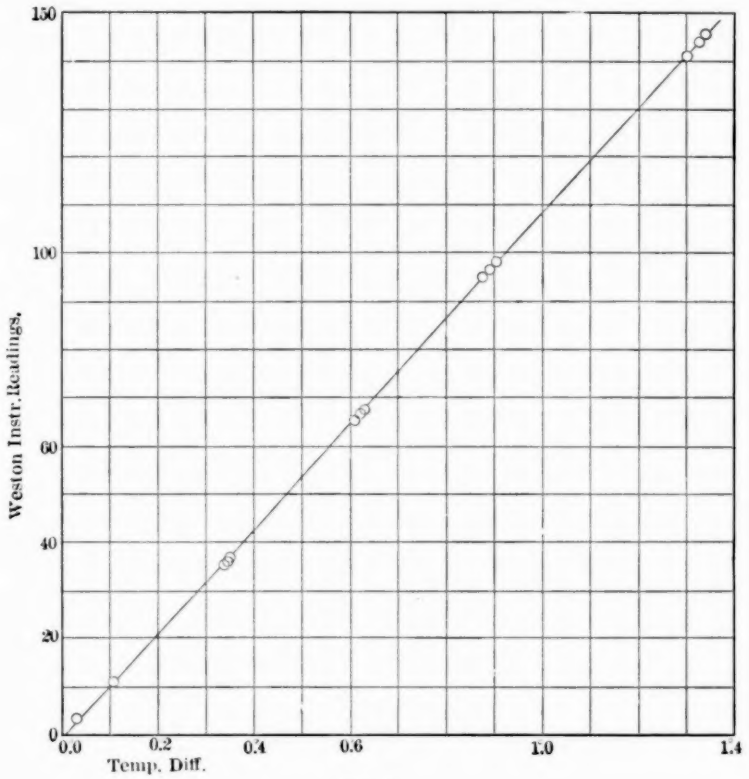


Fig. 5.

sible. The fact that the curve does not pass through the origin of coördinates is easily explained by a change in the thermometer corrections after comparison ; with both junctions in the same mercury bath, with no current in the potentiometer and with the switch S properly closed no deflection of the galvanometer occurred. The working curve was therefore drawn to the same slope as the calibration curve and made to pass through the origin.

If w be used to represent the ammeter reading and τ the *difference* in the temperatures of the thermal junctions, the working curve is given by the equation

$$\tau = 0.00925 \cdot w$$

when the mean temperature, t, is 20°.3 C. Then from the work on the auxiliary couple we have

$$\left(\frac{w}{\tau}\right)_t = \left(\frac{w}{\tau}\right)_0 (1 + 0.00086_2 \cdot t).$$

From these we find that

$$\left(\frac{\tau}{w}\right)_0 = 0.00941$$

and therefore that

$$\left(\frac{\tau}{w}\right)_t = \frac{0.00941}{1 + 0.00086_2 \cdot t},$$

which enables us to transfer ammeter readings into temperature differences for any mean temperature. The sensitiveness of the ammeter, immediately after the calibration was completed, was found to be $5.83_6 \times 10^{-5}$ amp. per division. The sensitiveness was afterwards taken at intervals of several days; changes could be noticed (due apparently to weakening of the magnetic field) but they were so slight as not to affect the calibration.

After the calibration the collodion was dissolved from the junctions and these were put into their places in the nozzle.

In the manipulation of the apparatus three persons were necessary. It was the duty of the first to attend the control valve and by careful adjustment to maintain a constant pressure in the part beyond; the second person controlled the bath temperatures and read the thermometers and the pressure difference manometer; the third attended the galvanometer and ammeter readings.

In order to make a determination the baths were put into the proper condition, the pressure was brought to the desired value and the exit valve was opened until the pressure difference was about one atmosphere. The large water bath was kept as nearly as possible at constant temperature and the oil baths were brought to temperatures which were indicated from time to time by the elec-

trical readings. The time necessary for a determination varied from fifteen minutes to an hour; in several cases even a longer time elapsed before steady conditions were attained.

In general the pressure difference, under which a determination was made, was not exactly one atmosphere. Correction was made to this unit by assuming a proportionality of the thermal effect to pressure difference — a law firmly established by the work of Joule and Thomson and again by that of Natanson.

The control of temperatures of the oil baths was a source of difficulty — especially in the determination at 0° C., for at this temperature it was necessary to use a flow of cold salt water through copper tubes submerged in the oil and the control was not an easy one. However, a determination was continued until the proper temperature control had been maintained sufficiently long to insure either a negligible or a calculable error due to this source. To obtain data from which approximate errors could be estimated from known errors in the bath temperatures, large changes in these temperatures were intentionally made from time to time and the resulting effects upon the temperatures of the gas stream were noted.

Of all the determinations which were made, two or three were discarded because the necessary corrections would have been too serious; four of the others were corrected, one to the extent of 0°.015, the other three by amounts not exceeding 0°.010.

It might seem, on first thought, that serious error would be caused by conduction of heat through the porous plug and around the plug through the material of the nozzle. But this transfer is at most only a small thing, and moreover is of such character as to eliminate itself; for the heat given up by the gas stream between the lower thermal junction and the plug will be almost exactly equal to that taken up by the stream in the corresponding region above the plug (the symmetry is broken only by the thin layer of gas between the main body of the nozzle and the small tube of vulcanized fiber which holds the upper steel disk in place).

During the determinations at high temperatures it was necessary to heat the gas before it reached the large spiral in order that it might enter the nozzle at, or very nearly at, the temperature of the bath. The heating was accomplished by applying a Bunsen flame,

protected from air drafts, to the copper tube between the pressure equalizing cylinder and the bath. This method of heating cannot be made a very steady one and some fluctuations of temperature remained after the gas had passed through the spiral. The potentiometer settings were made more difficult on this account, but a steady watch was kept on the galvanometer behavior and it was found that the ammeter readings taken when the fluctuations were small were consistent with each other and also that at these times the difference between the temperature of the bath and that of the gas as it entered the nozzle was small.

RESULTS.

Determinations were first made at room temperature, the gas pressure being changed from one determination to another with the intention of finding the law of dependence of the thermal effect upon pressure. The results, as plotted from time to time, began to trace, with more or less certainty, a line parallel to the axis of pressures. The line was very nearly a verification of the results of last year, except that there was no indication of a decrease of pressure until a pressure of 41 atm. was reached. Here the result was considerably lower than those preceding. It was noticed however that the gas analysis, which was made at the end of the determination, indicated a higher percentage of impurity than any of the previous analyses had shown (see determination X. in the table below). It was then decided to delay the experiments and to make a search for purer gas.

The gas, which had been used up to this time, showed amounts of impurity varying from 4 or 5 per cent. (by volume), when taken from a full cylinder, to about 0.2 per cent. when from an empty one; the amount of impurity *gradually* decreased as the gas was used from the cylinders. Complete analyses of the gas were not made, but delicate tests for H_2S and for SO_2 gave negative results. These were considered possible components — the gas came from natural springs — and tests for them were essential because, if present, they would have been absorbed by KOH and would not have appeared as impurities in the partial analyses. Also a test for oxygen gave negative results, showing that the impurity was not air.

No better gas was found, however, and it was decided so to choose the cylinder, which was to furnish the gas for any determination, that two or more results could be obtained, at a given pressure and temperature, with amounts of impurity differing as widely from each other as possible. By this procedure a dependence of the thermal effect upon impurity could be determined, and the thermal effect for pure CO_2 could be found by extending the curves back to the axis of no impurity (see Fig. 6).

This was done and the results of the observations at various pressures and temperatures are contained in the following table. The gas

No.	Date.	Percentage Impurity.	Mean Pressure (atm.).	Mean Temperature.	Pressure Difference (cm. Hg).	Temperature Difference.	Same Corrected on Account of Bath Temperatures.	Temperature Difference per Atmosphere Pressure Difference.
XVI.	5/17	0.32	7.6	−0°.5	68.6$_6$	1°.31$_6$	1°.32$_6$	1°.46$_7$
XV.	5/11	0.32	7.6	−0 .6	71.1$_7$	1 .37$_1$		1 .46$_4$
XI	5/4	2.1	7.6	+0 .8	73.2$_0$	1 .32$_8$		1 .37$_9$
								1.39$_6$ at −0.6
XII.	5/9	0.28	14.4	−0 .4	69.6$_0$	1 .34$_6$		1 .47$_0$
XIV.	5/11	0.75	14.4	−0 .6	69.4$_8$	1 .34$_3$	1 .32$_8$	1 .45$_5$
XVII.	5/17	0.20	21.2	−0 .6	69.1$_5$	1 .33$_2$		1 .46$_4$
XIII.	5/9	0.72	21.2	−0 .6	72.7$_0$	1 .36$_9$		1 .43$_1$
XVIII	5/18	1.7	26.4	−0 .5	71.2$_0$	1 .36$_3$	1 .36$_7$	1 .45$_0$
II.	4/19		7.6	20 .4	76.7$_3$	1 .19$_9$		1 .18$_8$
VII.	4/20	1.5	7.6	20 .4	74.5$_8$	1 .14$_0$		1 .16$_1$
VIII.	4/25	0.23	10.8	20 .5	73.6$_9$	1 .16$_1$		1 .19$_7$
III.	4/19		14.4	20 .4	76.1$_7$	1 .17$_0$		1 .16$_7$
IV.	4/19	0.20	21.2	20 .4	76.5$_8$	1 .17$_7$		1 .16$_8$
V.	4/19		25.2	20 .4	75.7$_6$	1 .18$_6$		1 .19$_0$
IX.	4/25	0.89	27.4	20 .4	76.1$_2$	1 .16$_4$		1 .16$_2$
XXI.	5/19	0.24	34.2	20 .4	71.1$_3$	1 .11$_8$		1 .19$_4$
XIX.	5/19	1.1	34.2	20 .4	76.8$_8$	1 .16$_4$	1 .17$_1$	1 .15$_7$
XX.	5/19	0.45	41.0	20 .4	75.3$_6$	1 .17$_4$		1 .18$_4$
X.	4/25	2.2	41.0	20 .4	75.8$_8$	1 .13$_2$		1 .13$_4$
XXII.	5/24	0.17	7.6	39 .5	75.2$_4$	1 .03$_3$ (?)	(Empty Cyl.)	1 .04$_1$ (?)
XXIV.	5/24	0.24	7.6	39 .5	76.3$_0$	1 .04$_8$		1 .04$_4$
XXIII.	5/24	2.1	7.6	39 .5	75.5$_0$	1 .02$_0$		1 .02$_7$
XXX.	6/2	0.22	14.4	59 .5	76.2$_5$	0 .95$_6$		0 .95$_3$
XXVI.	5/26	1.3	14.4	59 .5	75.1$_4$	0 .93$_3$		0 .94$_4$
XXIX.	6/2	1.3	14.4	59 .5	76.1$_6$	0 .95$_0$		0 .94$_8$
XXXI.	6/15	0.42	14.4	79 .5	74.3$_9$	0 .85$_0$		0 .86$_8$
XXXIII.	6/16	0.20	14.4	96 .6	74.0$_0$	0 .74$_7$		0 .76$_7$
XXXII.	6/16	1.8	14.4	96 .5	77.1$_4$	0 .82$_2$		0 .80$_6$

presures and temperatures tabulated in it are the averages of the two values of each on the two sides of the porous plug. The last column gives the corrected thermal effects — corrected where necessary, on account of errors in one or the other of the bath temperatures, and also on account of the pressure-differences. These cor-

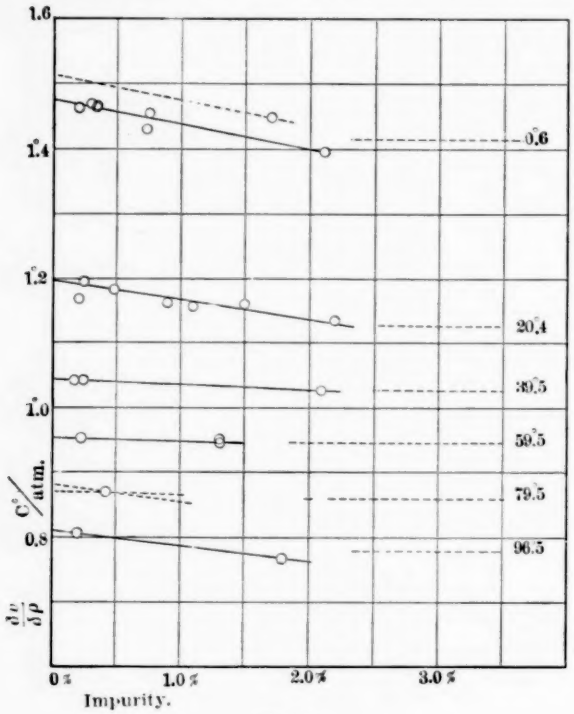


Fig. 6.

rected values are plotted as ordinates of Fig. 6 with corresponding percentages of impurity as abscissas. The values of the thermal effect for pure CO_2 as indicated by the lines of Fig. 6 are then plotted as ordinates in Fig. 7, with corresponding temperatures as abscissas.

For the results obtained at 20° C. the lines of Fig. 6 intersect the axis of no impurity at nearly the same point for all pressures, 41 atm. being the highest pressure reached at this temperature. All except three of the results obtained at 20° are plotted in Fig. 6. No analyses of the gas were made for them (they were obtained before any serious dependence upon impurity was suspected). The

determination at 0° C. exhibited the same peculiarity until a pressure of 26 atm. was reached. The result at this pressure gives a point on the impurity diagram considerably above the line which shows the dependence of the thermal effect upon impurity. In the

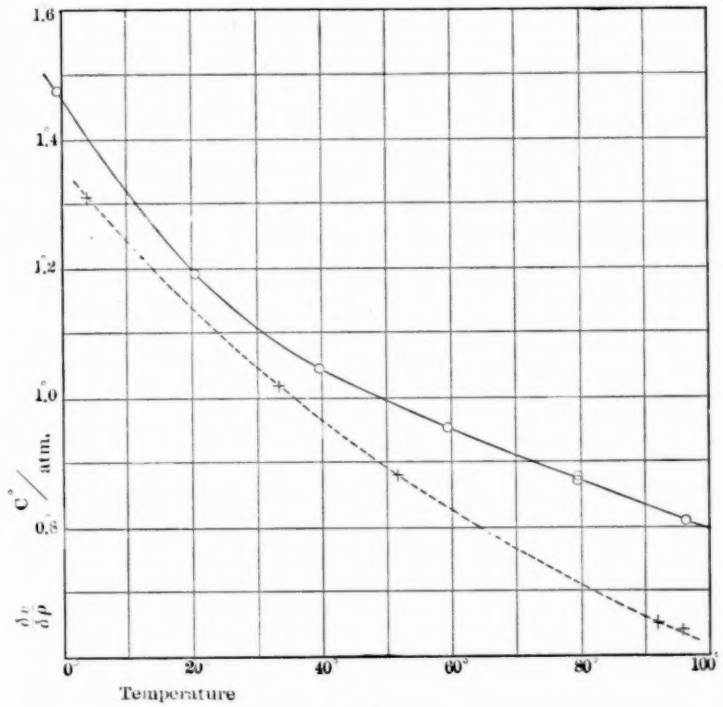


Fig. 7.

results taken, both at 20° C. and 0° C., there seemed to be no regular dependence of the effect of impurity (upon the observed thermal effect) upon pressure. Accordingly the thermal effect for pure gas at 26 atm. pressure was assumed to be that indicated by a line drawn parallel to the line which represents the other results at the same temperature.

Several trials were made at 0° C. to reach higher pressures than this. CO_2 condenses at about 35 atm. when its temperature is 0°, and it had been hoped that determinations could be carried to within 3 or 4 atm. of this point. The behavior of the electrical circuits seemed to indicate that condensation of the gas occurred at the con-

trol valve, due to the severe cooling there. If this did occur it was, of course, present also in the case of determinations under high pressures at 20° C.; but at 20° the large copper spiral was able, probably, to cause a complete re-evaporation of the small globules of liquid. The determination at 26 atm. was made possible only by the application of a Bunsen flame to the copper tube just in front of the valve. Very likely the use of a spiral heating tube at this point would have made work at higher pressures possible, but, with the determinations at higher temperatures still to be made, there was no time for the necessary changes.

Of the three results obtained at 80° C. only the last one was kept. The other two were obtained under such unfavorable heating conditions that the behavior of the electrical part of the apparatus did not insure a great amount of confidence in them. The simple application of a Bunsen flame to the small copper tube just in front of the large water bath was found to be quite satisfactory in the determinations at 40° and at 60°, but when the heating became as vigorous as was necessary at 80°, this alone was not satisfactory. The behavior of the apparatus indicated serious irregularities in the effect of the flame, due perhaps to the fact that the gas in passing through the tube came more and less thoroughly into contact with the heated walls. With this explanation in view a corresponding remedy was applied. A length of 25 or 30 cm. of the tube at this place was filled with lathe turnings which served to stir the gas as it passed through the heated portion. With this precaution the observations at 80° and at 97° were fully as satisfactory as those at 60° had been.

An attempt was made, after the determinations at 97° were obtained, to add others at 80°, but a series of mishaps rendered these impossible. The most serious was the development of leaks at the nozzle, caused by the change from a high temperature to a lower one — the lead packing has a much greater coefficient of expansion than the steel of the nozzle. A repair of the leaks made necessary the removal of the thermo-electric junctions, but the plugs which carried them had become so firmly fixed in their places by the action of the high temperatures upon the packing materials that one of them was broken. This made even a recalibration of

the junctions impossible. Determinations were discontinued. I may state here — merely as a fact of observation — that all of these accidents occurred while I was using the thirteenth cylinder of gas.

Since only one satisfactory determination was obtained at 80° the best indication, obtainable from it as to the magnitude of the thermal effect for pure gas at this temperature, is that given by the pair of dotted lines, drawn through the point which represents it in Fig. 6, one parallel to the line of results at 60° the other parallel to that at 97°. With this treatment the absence of other results at 80° increases the uncertainty (already present on account of errors of observation and of control) by an amount less than 0°.01.

The variations in the slope of the impurity lines from one temperature to another is a source of considerable concern. The indication of the results up to 60° is that the effect of the impurity becomes less as the temperature increases, but the line of results at 97° does not fulfil this indication. An interpretation of the variation of slope of the lines is offered by the results at 0° and at 20°. At either of these temperatures the determinations which were obtained with the purest gas are fairly consistent with one another — there is only one exception to this statement; result IV., taken at 20°, falls low. On the other hand the results at higher percentages of impurity are not consistent; especially is this true at 0°. So far as records of the determinations are concerned the latter results are just as trustworthy as the others. An attempt to represent the effect of impurity at each of the various pressures, say at 0° C., results in a series of lines whose slopes differ almost as much as do the slopes of the lines from one temperature to another. The only interpretation, then, which the results warrant, is that the impurity is not the same gas or gases in the various determinations. Unfortunately a complete analysis of the impurities was not made for each sample of gas taken from the apparatus. It is fortunate, however, that for almost all temperatures, results were obtained with very pure gas; the distance over which extrapolation is necessary in order to determine the thermal effects for pure gas is not a great one; the errors introduced by the uncertainty in the slope of the lines are, therefore, not serious.

The dependence of the thermal effect upon impurity is a part of an entirely separate problem — that of the Joule-Thomson effect in mixtures of gases — upon which some work was done by Joule and Thomson themselves. I hope to be able to take up this problem, with such modifications of the present apparatus as will be necessary, in order to verify and to make more complete the experimental results at present available. Recent developments in the theory of gas mixtures have made work in this region even more important scientifically than it was in the past century.

In a discussion of the results of the present research it is necessary to call attention to discrepancies between them and the results of previous researches. The preliminary results of last year are not wholly in accord with those of this year. The line

$$\frac{\delta\vartheta}{\delta p} = 1^{\circ}.19 - 0.0015 \cdot p$$

which was found to represent those obtained last year at 22° C. indicates values for low pressures which are tolerably consistent with the indication of the curve of Fig. 7 for the same temperature. For high pressures the discrepancies are serious and in view of the facts that, in the preliminary work, the amounts of impurity in the gas were not followed closely and that it was impossible to maintain proper temperature control about the nozzle, it is necessary to discard the results of last year in comparison with the present ones.

Considering then the work of Natanson, whose determinations were all made at room temperature (20° C.) and at pressures ranging from 1.5 atm. to nearly 25 atm., it is to be noticed first that the equation, given by him as a representation of his results,

$$\frac{\delta\vartheta}{\delta p} = 1^{\circ}.18 + 0.0126 \cdot p_m$$

where p_m is the average value of the pressures on the two sides of the porous plug, really does not represent them fairly. The values of the thermal effect plotted as ordinates, with corresponding values of p_m as abscissas, trace with considerable certainty a curved line which starts at about 1°.23 and rises, with steadily increasing slope as the pressure increases, to a value of about 1°.50 at 25 atm.

This very marked dependence upon pressure is not verified by the results of the present research. In the determinations made this year no dependence upon pressure was shown by the results at 20° although the pressure was carried as high as 41 atm.; and at 0° no dependence was found until a pressure of 26 atm. was reached; here the result indicated an increase in the thermal effect over the values at lower pressures. The result just mentioned is isolated and was, moreover, obtained under considerable difficulty; its indications must therefore, in all fairness, be rated as somewhat doubtful. However, in another paper further experimental evidence, deduced from Andrews' work on the compressibility of CO_2, will be given, which will tend to indicate again that such a change is altogether probable at this pressure.

To account for the discrepancy between Natanson's results and my own is not easy. There appears to be only one explanation and that is not entirely satisfactory; it rests upon the fact that, in his apparatus, the large copper tube, through which the gas passed before reaching the porous plug, was closely packed with lathe turnings in order to provide greater surface with which the gas would be brought into contact. The use of more turnings than are sufficient to bring the gas thoroughly into contact with the wall of the tube would seem, however, to be detrimental; there is very little chance for conduction of heat into the interior of the tube by the turnings for they touch the walls and each other only in small points; moreover, if the packing of these turnings was as close as Natanson's description indicates, it is to be expected that a fall of pressure would result from the obstruction offered to the flow of gas, and a fall of pressure means a Joule-Thomson effect of corresponding magnitude. If, therefore, some cooling of the gas, due to this cause, did occur, in all probability the gas entered the plug at a temperature lower than that of the bath, for it is not to be expected that the bath could remove the effects of the fall of pressure which occurred in the last end of the tube. Whether or not such an explanation will account for the total apparent increase in the thermal effect observed by Natanson and for the form of curve, which his results trace, cannot be determined.

In order to compare more readily the results obtained by Joule

and Thomson with those of the present piece of work I have copied theirs in the following table ; the results are corrected, however, to the basis of 1 atm. difference in pressure above and below the porous plug. The corrections, which had already been made by them, covered errors due to influence of the bath upon the gas stream and reduced the observed thermal effects to the basis of pure CO_2. The latter was made on the assumption that each component of the mixture maintained its own individual thermal effect and was entirely independent of the other component ; this assumption was not considered by them to be a correct one — in fact it had been proven experimentally to be false — consequently the last column of the table cannot be considered to be completely corrected. The dotted line of Fig. 7 represents these results.

The Joule-Thomson Results.

Gas Components.		Bath Temp.	Press Diff. in. (Hg).	Obs. Cooling Effect.	Mean Temp.	Corrected Cooling Effect. (1 atm.)
CO_2.	Air.					
96.5 %	3.5 %	7°.4	164.1	6°.72	4°.0	1°.31
98.2	1.8	35 .6	127.5	4 .19	33 .5	1 .02
99.2	0.8	54 .0	146.0	4 .18	51 .9	0 .88
97.9	2.1	93 .5	167.2	3 .42	91 .8	0 .65
98.3	1.7	97 .5	151.0	3 .11	95 .9	0 .64

The discrepancies between these results and my own are very pronounced throughout the range of temperatures used, but are especially so at the higher temperatures. It is at once evident that the incompleteness of the corrections for impurity cannot explain such differences ; if, however, data for completing these corrections were available the gap would be narrowed by the process.

In the present apparatus there seems to be only one possible explanation of the discrepancies. There is a possibility of a flow of gas from the region below the porous plug to that above by another path than the porous plug itself. A screw packing (not shown in Fig. 2 on account of complication of the drawing) was provided around the middle of the vulcanized fiber nozzle — between it and the surrounding steel cylinder — in order to prevent any gas from leaving the lower region by flowing outward along the plug which carries the lower thermal junction, then upward between the fiber nozzle and the steel cylinder, and into the main

gas stream again, along the plug, which carries the upper junction. Any flow of gas through this packing would be a diffusion process and, if adiabatic, would not affect the accuracy of results; however there is danger that such a flow may be far from adiabatic in character. At high temperatures that part of the steel cylinder between the two oil baths is exposed to air which is lower in temperature than the baths; the error would, therefore, increase the observed cooling effect. This explanation will not account for the discrepancies between the two curves at low temperatures. Moreover the danger here is not as great as it seemed, at first glance, to be. The part of the apparatus from the top rim of the barrel to a point above the upper oil bath was enclosed in heavy wrappings of cloth and the air temperatures in this enclosure, even at points some distance from the baths, were only ten or fifteen degrees below the bath temperatures. The protection of this part of the steel cylinder from the surrounding air is better than the drawing of Fig. 2 indicates; the flange on the bottom of the upper oil cup is deeper than is there shown; it extended, in the determinations at low temperatures, to within a short distance of the oil in the lower bath, and in those at 80° and 97° the hot oil softened the rubber ring, which supports the upper cup, so that it moved down and rested on the steel ring which holds the lower thermal junction in place. Furthermore there is considerable experimental evidence leading to the conclusion that errors from this source were not serious; *e. g.*, when the results were compared and this source of error was under consideration, it was thought that an explanation could be found here for the change in slope of the impurity line at 97° (Fig. 6). Errors in temperature of the oil baths would have had considerable influence upon that part of the gas which may have flowed along this by-path. But the records of the observations at this temperature show that such errors in bath temperatures as were present and also the change in temperature of the air in the enclosure under the cloth wrappings would have had a tendency to decrease the slope of this line rather than to increase it. Finally an examination of the packing, described above, after the apparatus was dismounted, showed that it was hard and firm, and, although it is impossible to say that no gas leaked around by this path, all available facts indi-

cate that the amount was not such as would seriously affect the results.

On the other hand, there are, in the Joule-Thomson determinations, two possible sources of error which may account for the discrepancies between the two sets of results. A study of the descriptions and drawings of their apparatus shows a possibility that the gas pressure above the porous plug was not barometric pressure as they assumed it to be; the gas, after it escaped from the plug, passed through a pipe into a gas holder. The dimensions of this pipe are not given, but from the drawings of their apparatus and from descriptions of other parts I judge that it was a 2-in. pipe; the length is altogether uncertain. There was, moreover, at one point of the pipe a large stop-cock — dimensions uncertain. In view of the fact that the stream velocities varied from 2 to 3 feet per second (assuming the pipe 2 inches in diameter) it seems possible that some appreciable fall in pressure occurred in this pipe and stop-cock. An excess over barometric pressure would have made the pressure difference, under which an experiment was performed, less than that which their mercury pressure gauge indicated. A more serious error would result from the effect of pressure upon the reading of the thermometer which was placed in the gas path just above the porous plug. Each of the errors resulting from this cause would make the apparent thermal effect (reduced to a pressure difference of 1 atm.) smaller than the true value. The other possible source of error is brought to one's notice by the fact that Joule and Thomson make no mention of having applied a stem correction to the readings of the thermometer which measured the temperature of the large water bath. This bath temperature was assumed by them (correctly, since in their apparatus the large copper tube in the bath was 60 feet long and 2 inches in diameter) to be the temperature of the gas as it entered the porous plug. But the thermometer, which measured the bath temperature, was so placed that its bulb was near the nozzle and in the observations at high temperatures must have had a considerable length of its stem and of mercury thread exposed to air at a temperature far below that of the bath. The thermometer would have read too low and, if no stem corrections were applied, the observed thermal

effect would have been too small. None of the discrepancies between their results and mine is too large to be accounted for by reasonable assumptions as to the magnitude of these two possible errors in their observations.

In addition to the acknowledgments in the introduction of this paper I wish to acknowledge my hearty thanks to Dr. S. R. Cook, Mr. C. W. Waggoner, Mr. L. Howe and especially to Mr. H. J. Lathrop for help in taking observations during the work of this year.

In a later paper I shall show that it is possible to separate the thermal effects, measured in this research, into the two essential parts, one due to the external work which is done by the gas, the other — the pure Joule effect — due to the work done against the forces of intermolecular attraction; for this separation the available data on the compressibility of CO_2 will be used. The theoretical treatment of the results — their bearing upon the various characteristic gas equations, the possible development of such an equation for this gas, the deduction of a law of molecular attraction — will also be given in that paper.

Summary.

The porous plug form of apparatus was used in this piece of work. The difference between the pressures on the two sides of the plug was about 1 atm. for all of the determinations. The differences in temperatures, (1) of the gas before and after passing through the plug, (2) of the gas and of the large water bath, which surrounded the copper heating (or cooling) tube, were measured by thermo-electric junctions; the thermo-electro-motive forces were measured by a modified potentiometer method.

In order to obtain the magnitude of the cooling effect for pure CO_2, determinations were made at a given temperature and at a given pressure with gas containing various percentages of impurity and these results were then extrapolated for pure CO_2. At 0° C. the results of such extrapolation show no dependence of the thermal effect upon pressure until a pressure of 26.4 atm. is reached; the one result obtained here indicates an increase over the values observed at lower pressures. At 20° C. the thermal effect

is independent of pressure as far as observations were carried; 41 atm. was the highest pressure reached at this temperature. The dependence of the cooling effect upon temperature is shown by the full line of Fig. 7; for purposes of comparison the results of the Joule-Thomson determinations for CO_2 are also represented in this figure, by the dotted line.

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